INTERMOLECULAR INTERACTION FOR POLAR AND NONPOLAR MOLECULES CORRELATED WITH PROPERTIES OF GASES

By

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To My Parents

PREFACE

Since the establishment at the turn of this century
chemical engineering has steadily kept pace with the
progress in other branches of science and engineering.
The advances in molecular physics put those elegant
molecular concepts at the disposal of chemical engineers.
Thus they are able to relate macroscopic properties of
substances to microscopic molecular properties to obtain
many useful correlations and better design procedures that
can be utilized in their challenging tasks. The statistical
mechanics enables them to interpret all the thermodynamic
and transport properties of materials in terms of inter-
molecular forces. Indeed the intermolecular forces play
highly important roles in this area. Much has been known
but much has yet to be known about these intermolecular forces.

In this work we are primarily concerned with the
prediction of properties of polar and nonpolar gases by
means of intermolecular potential energy functions. In
Chapters I and II the hard-core Morse potential is investi-
gated for nonpolar molecules in an effort to find a potential
model which can be applied to polyatomic as well as monatomic
molecules. In Chapters III through V the angle-averaged
potential model with the temperature-dependent parameters

are employed to correlate properties of polar gases and mixtures containing polar component. The parameters of this model are estimated from the critical temperatures and polarizabilities. In Chapter VII transport properties of gases are predicted from saturated liquid densities through the principle of corresponding states.

The reader is assumed to be no novice on the subject. It is intended that each chapter is complete in its entirety. Therefore no exhaustive review is included. Instead, each chapter has its own brief introduction at the beginning and full discussion and conclusion in the course of the chapter. However, all the chapters are closely related to one another.

The author wishes to express his appreciation to Dr. K. E. Gubbins for serving on the committee. He is especially indebted to Dr. T. M. Reed who directed this research and served as the chairman of the supervisory committee. He is also responsible for influencing the author to wander in the jungle of "Molecular Chemical Engineering ."

                                        Jae Ho Bae

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a   Radius of spherical core in the hard-core Morse potential.

a*   Reduced core radius defined by Eq. (3).

a_j Variable defined by Eq. (9).

A   Variable defined by Eqs. (37) or (48).

$\overline{A}$ Variable defined by Eq. (16).

$\underline{A}$ Positive constant defined by Eq. (58).

b   Variable defined by Eq. (18).

B   Second virial coefficient. Subscripts refer to temperatures.

$\overline{B}$ Variable defined by Eq. (17).

$\underline{B}$ Positive constant defined by Eq. (58).

B*   Reduced second virial coefficient. Subscripts refer to temperatures.

c   Constant in the hard-core Morse potential model.

C_p Molar heat capacity.

C_p^o Molar heat capacity at zero pressure.

D   Diffusion coefficient.

D*   Reduced diffusion coefficient defined by Eq. (57).

$D^{\neq}$ Reduced diffusion coefficient defined by Eq. (62).

f_I Factor defined by Eq. (25).

f_d Factor defined by Eq. (26).

g(x)   Function defined by Eq. (12).

k   Boltzman constant.

m   Attraction exponent of the n-m potential. Reduced
    molecular weight in Eq. (45).

M   Molecular weight.

n   Repulsion exponent of the n-m potential. Maximum
    number of summation in Eq. (8).

N   Avogadro number.

P   Pressure.

Q   Variable defined in Chapter IV.

r   Intermolecular separation.

$r*$ Intermolecular separation at minimum potential energy.

$r*_m$ Reduced separation at minimum potential energy defined
    by Eq. (4).

r^o Temperature-independent distance parameter in the
    12-6-6 model.

S   Variable defined in Chapter IV.

t   Temperature.

T   Absolute temperature.

T*   Reduced absolute temperature defined by Eq. (7).

$T^{\neq}$ Reduced temperature defined as $T\underline{B}/A$.

U   Intermolecular pair-potential energy.

U*   Reduced intermolecular pair-potential energy defined
    by Eq.(2).

V   Molar volume.

x   Variable defined by Eq. (10). Subscripted variables
    refer to mole fraction.

X   Variable defined in Chapter IV.

Y   Variable defined in Chapter IV

Z   Number of electrons in an atom or a molecule. Variable
    defined in Chapter IV.

α Polarizability.

α_T Thermal diffusion factor.

β $1/kT$

δ Constant defined by Eq. (55).

ϵ Minimum potential energy at r_m.

ϵ^* Temperature-dependent energy parameter in the 12-6-6 model.

ϵ^o Temperature-independent energy parameter in the 12-6-6 model.

η Viscosity. Subscripts refer to temperatures.

η_m Viscosity of mixture.

η^* Reduced viscosity defined by Eq. (56).

$\eta^{\neq}$ Reduced viscosity defined by Eq. (61).

μ Dipole moment.

$\overline{\mu}$ Joule-Thomson coefficient.

$\overline{\mu}_o$ Joule-Thomson coefficient at zero pressure.

ρ Molar density.

σ Intermolecular separation at zero potential energy.

$<\phi>$ Angle-averaged pair-potential energy.

Ω Collision integral.

Subscript
  c   Critical values.

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MOLECULES CORRELATED WITH PROPERTIES OF GASES

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August, 1966

Chairman: T. M. Reed
Major Department: Chemical Engineering

This work is concerned with the pair-potential
energy functions for the prediction of thermodynamic and
transport properties of polar and nonpolar gases.

The defect in the Morse potential energy function
of the finite value at zero separation is avoided by assigning
spherical cores to molecules. Tables for the classical
second virial coefficient on this model are given. The
potential parameters for ten nonpolar molecules are determined
from the experimental second virial coefficients. The experi-
mental data are reproduced very well and the agreement is
comparable with other potentials. This model is also extended
to 12 binary gas mixtures for which the second virial coeffi-
cients are predicted quite adequately.

For polar molecules the transport properties of
dilute gases are reproduced accurately by the 12-6 pair-
potential energy function with temperature-dependent para-
meters, $\varepsilon *$ and $r*$. These parameters are defined from the

classical electrostatic point dipole-dipole and dipole-induced dipole interactions by statistical averaging over the relative orientations of the molecules, and adding nonpolar attraction and repulsion terms. The model is also applied to binary mixtures of a polar and a nonpolar gas with parameters determined from the experimental viscosities. With simple combining rules for unlike interaction the calculations of viscosity, diffusion and thermal diffusion factor show very good agreements between experimental and calculated values. The usual 12-6 Lennard-Jones integral tables are used with the temperature-dependent parameters.

The parameters are also determined for this model from the second virial coefficients of polar gases. The validity of these parameters is further confirmed by computing the Joule-Thomson coefficients at zero pressure for several molecules.

The quantum mechanical expression of Mavroyannis and Stephen for dispersion attraction confirms the empirical values obtained for the nonpolar or dispersion attraction constant for small polar and nonpolar molecules. From this expression and the principle of corresponding states a method of estimating the parameters of above model is devised. The estimated parameters give reasonable results in the calculation of both thermodynamic and transport properties of polar gases.

The transport properties of nonpolar gases are
correlated with the saturated liquid density parameters
through the principle of corresponding states. Thus
viscosity and diffusion coefficients are predicted within
experimental error for simple molecules.

CHAPTER I

HARD-CORE MORSE POTENTIAL FOR THE
SECOND VIRIAL COEFFICIENTS

Most of the potential models available for nonpolar
molecules predict the second virial coefficient quite
accurately over a reasonable temperature range. However,
the accuracy becomes worse as the molecules become large
and nonspherical. In an effort to find a potential which
can be used for large nonspherical as well as for the
spherical molecules, the hard-core Morse potential is
investigated in this chapter.

The empirical Morse potential, originally proposed
for the chemical bond energies by Morse,[1] was successfully
employed for the second virial coefficient by Konowalow,
et al.[2,3] Saxena and Gambhir[4] extended the model to
the binary mixtures. Saxena and Bahethi,[5] Gambhir and
Saxena[6] and Saran[7] used the model for the correlation
of transport properties of dilute gases.

In the hard-core Morse potential the convex core
model of Kihara[8] is combined with the Morse potential.
Thus the potential energy of interaction is assumed to
depend on the shortest distance between core surfaces and
to be the functional form of the Morse potential. The

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convex core can have any shape but only the spherical core is considered here. The potential is:

$$U(r) = \begin{cases} \varepsilon\left\{\exp\left[-\left(\frac{2c}{\sigma-2a}\right)(r-r_m)\right]-2\exp\left[-\left(\frac{c}{\sigma-2a}\right)(r-r_m)\right]\right\}, & r > 2a \\ \infty & r \stackrel{<}{=} 2a \end{cases} \quad (1)$$

where a is the core radius. σ is the separation at zero potential energy, ε is the minimum potential energy at r_m and r is the separation between the core centers. The constant c has the same meaning as in the Morse potential. In reduced form we have:

$$U^*(r^*) = U/\varepsilon = \begin{cases} \exp\left[-2c(r^*-r_m^*)\right]-2\exp\left[-c(r^*-r_m^*)\right], & r^* > a^* \\ \infty & r^* \stackrel{<}{=} a^* \end{cases} \quad (2)$$

where

$$\left.\begin{aligned} r^* &= \frac{r}{\sigma-2a} \\[2em] a^* &= \frac{2a}{\sigma-2a} \end{aligned}\right\} \quad (3)$$

It can be easily shown that the reduced separation at the potential minimum is:

$$r_m^* = 1 + a^* + (1/c)\ln 2 \quad (4)$$

Eq. (4) shows that r_m^* of this model is the sum of r_m^* of the Morse potential and the reduced core radius. In fact Eq. (2) is in exactly the same form as that of the Morse

potential except it is displaced by the distance a*.

According to classical statistical mechanics the second virial coefficient for angle-independent potentials is written as:

$$B(T) = 2\pi N \int_0^\infty (1-e^{-U\beta}) r^2 dr \qquad (5)$$

where N is the Avogadro number, β is $1/kT$, and k is the Boltzmann constant. By the substitution of Eq. (2) into Eq. (5) and partial integration we get B(T) in reduced form as follows:

$$B*(T*,c,a*) = a*^3 + 3 \int_{a*}^\infty (1-e^{-U*/T*}) r*^2 dr* \qquad (6)$$

where
$$B* = B / \left[\frac{2}{3} \pi N (\sigma - 2a)^3 \right]$$

$$T* = kT/\varepsilon \qquad\qquad\qquad\qquad \left.\right\} \quad (7)$$

To perform the numerical integration the Gauss-Mehler quadrature[9] was employed. It is given by:

$$\int_{-1}^{+1} f(r)(1-r^2)^{-1/2} dr = \frac{\pi}{n} \sum_{j=1}^{n} f(a_j) \qquad (8)$$

where
$$a_j = \cos\left(\frac{2j-1}{2n}\pi\right) \qquad (9)$$

This formula is accurate and simple to use.[10,11]   In

order to facilitate its use we introduce a new variable.

$$x = \frac{1+a^*}{1+r^*} \tag{10}$$

Then Eq. (6) becomes:

$$B^*(T^*,c,a^*) = a^{*3} + 3 \int_0^{+1} g(x)(1-x^2)^{+ 1/2}(1-x^2)^{-1/2}_{dx} \tag{11}$$

where

$$g(x) = (1-e^{-U^*/T^*})(1+a^*-x)^2 \left(\frac{1+a^*}{x^4}\right) \tag{12}$$

$$U^*(r^*) = \exp\left[-2c\left(\frac{1+a^*}{x} - 1 - r_m^*\right)\right] - 2\exp\left[-c\left(\frac{1+a^*}{x} - 1 - r_m^*\right)\right] \tag{13}$$

Since r^* or x represents the distance, $g(x)$ can be regarded as an even function. Finally, by Eqs. (8) and (9) we obtain:

$$B^*(T^*,c,a^*) = a^{*3} + \frac{3\pi}{n} \sum_{j=1}^{n/2} g(a_j)\sin\left(\frac{2j-1}{2n}\pi\right) \tag{14}$$

The calculations were carried out on the computer and the values of $B^*(T^*,c,a^*)$ are given in Appendix. For most cases $n = 60$ was sufficient to give one part per thousand accuracy but for the extreme cases, e.g., small T^*, large c and large a^*, n up to 200 was used. The accuracy is believed to be far better than one part per thousand for most of the values. The computer program was checked with $a^* = o$ in which case the model reduces to

the Morse potential. The result showed a complete agreement with the existing tables[2] for all the values of T^* and c.

Potential parameters for ten nonpolar molecules were determined from empirical second virial coefficients. At first the parameters were approximated by a graphical method originally used by Lennard-Jones.[12] They were then further refined on the computer by the least-squares fit.[13] It was assumed that the errors associated with second virial coefficients can be described by a Poisson distribution. Thus a weight, the inverse of the observed $B(T)$ value, was given to each point. The results are given in Table 1 where the four potential parameters, number of data points used, temperature range of the data, root-mean square deviation and references to the data are given.

The validity of the parameters depends on the temperature range and accuracy of the data. With the four parameters of the present model the data in a narrow temperature range can be fitted to several sets of parameters. Among the molecules considered here the reported data on C_3H_8, $n-C_4H_{10}$, and SF_6 were not consistent. Thus some sets of data were arbitrarily discarded. The fit was made with those data to which references are given in Table 1. Also a few data points were arbitrarily rejected when they differed from the calculated values by more than three times the rms deviation. They are indicated in Table 1.

The intermolecular attraction potential derived from dispersion theory[14] is a power series in r^{-1}. Dymond, Rigby and Smith[15] obtained an empirical two parameter potential as a polynomial in r^{-1} for the inert gas molecules, and quasi-spherical polyatomic molecules. An inconsistency of the Dymond-Rigby-Smith model is that the parameters obtained for the twelve molecules examined by those authors do not fit the requirements of the corresponding states theorem with respect to reduced critical constants for such a potential function. The Morse potential is implicitly a polynomial in r^{-1} with three parameters.

A difficulty with the Morse potential is that at $r = o$ the potential has a finite value. Thus at high temperatures molecules on collision pass through one another. This defect is overcome by the introduction of an impenetrable spherical hard core, the size of which is a fourth parameter, to give the hard core Morse potential.

The parameters given in Table 1 are reasonably consistent among themselves. As the molecular size increases the value of c increases, which corresponds to the narrowing of the reduced potential well. The values of ε/k are always larger than those obtained for other potentials.[16,17] Compared with those for other hydrocarbons considered, the value of ε/k for CH_4 seems too small, but the rms deviation is much less than that for other molecules. Also the core sizes of the molecules are somewhat large compared with

those of Kihara potential. For example, Sherwood and Prausnitz[16] obtained the core sizes of 0.1841 Å for Ar and 0.7309 Å for CO_2 while in this calculation we obtained 0.6738 Å and 1.0366 Å for Ar and CO_2, respectively. Considering the structure of the molecules the former values seem too small. Since the present model has a finite potential energy at r = 2a, it must have larger values of a and σ than those of the Kihara potential to have the same repulsion contribution to the second virial coefficient. The core sizes are inconsistent among Ar, Kr, SF_6 and neoC_5H_{12}.

The rms deviations between calculated and experimental second virial coefficient are comparable with those of other potentials for simple molecules.[16] However, for the hydrocarbons this model gives better agreement than the unmodified Morse potential.[17] Nevertheless, the second virial coefficients alone are not sufficient to determine the unique values of the four parameters. As with other potential functions,[18] it was possible to find several sets of quite satisfactory parameters.

With four adjustable parameters, the model is very flexible and from the results of this calculation it can be concluded with fairness that the model can be applied to the nonpolar molecules with good accuracy. For more thorough comparison between potential models the calculation of transport properties for the present model is highly desirable.

CHAPTER II

SECOND VIRIAL COEFFICIENT OF BINARY GAS MIXTURES
ON THE HARD-CORE MORSE POTENTIAL

The hard-core Morse potential of Chapter I is
extended to mixtures of gases since there exist many
experimental data on the second virial coefficient of
binary gas mixtures.

In order to approximate the potential parameters
for the unlike-pair interaction from the parameters for
the like-pair interactions combining rules for the parameters
should be used. The hard-core Morse potential can be
written in the form:

$$U(r) = \overline{A} \, e^{-2br} - \overline{B} \, e^{-br} \tag{15}$$

where

$$\overline{A} = \varepsilon \exp\left(\frac{-2c r_m}{\sigma - 2a}\right) \tag{16}$$

$$\overline{B} = 2 \, \varepsilon \exp\left(\frac{-c r_m}{\sigma - 2a}\right) \tag{17}$$

$$b = \frac{c}{\sigma - 2a} \tag{18}$$

and all the symbols have the same meaning as before. From
the theoretical considerations of Zener[19] the parameter

b for an unlike interaction can be obtained by:

$$b_{12} = \frac{1}{2} (b_{11} + b_{22}) \tag{19}$$

where subscripts denote interactions between molecular species. Unfortunately, no combining rules for the parameters $\overline{A}$ and $\overline{B}$ can be obtained from theory. Therefore, the empirical rules of Mason and Rice[20] and Saxena and Gambhir[4] are adopted for these parameters. Thus,

$$\overline{A}_{12} = (\overline{A}_{11}\overline{A}_{22})^{1/2} \tag{20}$$

$$\overline{B}_{12} = (\overline{B}_{11}\overline{B}_{22})^{1/2} \tag{21}$$

Since the cores are impenetrable, rigid, hard spheres, it is reasonable to use the arithmetic mean for the parameter a.

$$a_{12} = \frac{1}{2} (a_{11} + a_{22}) \tag{22}$$

From Eqs. (20) and (21) it follows:

$$\epsilon_{12} = (\epsilon_{11} \epsilon_{22})^{1/2} \tag{23}$$

The derivation of Eq. (23) is rather empirical but Eq. (23) is the common combining rule for 12-6 potential. Following Reed,[21,22] Hudson and McCoubrey,[23] and Mavroyannis and Stephen[24] we have:

$$\epsilon_{12} = (\epsilon_{11} \epsilon_{22})^{1/2} f_I f_s^6 \tag{24}$$

where

$$f_I = 2 \left(\frac{\alpha_1 \alpha_2}{Z_1 Z_2} \right)^{1/4} \Big/ \left[\left(\frac{\alpha_1}{Z_1} \right)^{1/2} + \left(\frac{\alpha_2}{Z_2} \right)^{1/2} \right] \qquad (25)$$

$$f_s = 2(V_{c_1}/V_{c_2})^{1/6} \Big/ \left[1 + (V_{c_1}/V_{c_2})^{1/3} \right] \qquad (26)$$

and α is polarizability, V_c is critical volume and subscripts denote molecular species. From Eq. (19) the following relationship is obtained:

$$\frac{C_{12}}{\sigma_{12}-2a_{12}} = \frac{1}{2} \left(\frac{C_{11}}{\sigma_{11}-2a_{11}} + \frac{C_{22}}{\sigma_{22}-2a_{22}} \right) \qquad (27)$$

Combining Eqs. (20) and (27) with the expression for r^*_m of Eq. (4) we obtain the combining rule for σ_{12} as follows:

$$\sigma_{12} = \left(\frac{C_{11}\,\sigma_{11}}{\sigma_{11}-2a_{11}} + \frac{C_{22}\,\sigma_{22}}{\sigma_{22}-2a_{22}} \right) \left(\frac{C_{11}}{\sigma_{11}-2a_{11}} + \frac{C_{22}}{\sigma_{22}-2a_{22}} \right)^{-1} \qquad (28)$$

Consequently Eqs. (22), (23) or (24), (27) and (28) give the desired combining rules for the parameters a_{12}, ε_{12}, C_{12} and σ_{12}.

The cross second virial coefficients are calculated for 12 binary gas mixtures. For the purpose of comparison calculations were made on the Morse potential and Lennard-Jones 12-6 potential whenever parameters were available. For the hard-core Morse potential the parameters in Chapter I were used and for other potentials the parameters

used are listed in Table 2. For the hard-core model the suggested combining rules are used and for the unmodified Morse potential the same rules are used with $a = o$ in which case Eq. (27) reduces to arithmetic mean for C_{12}. Saxena and Gambhir's combining rule for Morse potential implies implicitly the arithmetic mean for C_{12} even though they apparently did not notice it. For 12-6 potential model the usual geometric mean for energy parameter and arithmetic mean for size parameters are used. All the calculations were made with and without f-factors for ε_{12}, i.e., by Eqs. (23) and (24). The critical volumes and polarizabilities needed for f-factors are given in Table 3. The results which give better agreement to the experiments are summarized in Table 4. The cases when f-factors are used are indicated by a small f on the right side of the first row of that system.

For all 12 systems considered here the overall rms deviation in cc./mole is 8.56 and 11.44 for the hard-core model and the 12-6 model, respectively. For the five systems for which unmodified Morse potential is used, the deviation is 8.29, 5.13 and 9.80 for hard-core model, Morse and 12-6 potential, respectively. It is noted from this calculation that the two parameter Lennard-Jones potential is inferior to three parameter Morse potential or four parameter hard-core Morse potential.

The results show an apparent superiority of the unmodified Morse over hard-core Morse potential in the mixture calculations. However, with a close look, a definite conclusion cannot be drawn. It is well known that the second virial coefficient is not sufficient to determine unique values of several parameters of a potential model. The validity of the parameters depends on the temperature range and the accuracy of the data. It should be pointed out that for the Morse potential all the temperatures in the mixture calculations lie within the temperature range for which parameters were determined while for hard-core model this is not true.

Among the systems considered here $Ar + Kr$ is the only system for which the parameters for pure components were determined from the same data for both models. These systems show essentially the same results. For $CH_4 + Ar$, mixture calculations were made from $108.6°K$ to $295°K$ while CH_4 parameters of hard-core Morse potential were determined from the data of $273°K$ to $623°K$. At $295°K$ the calculated cross second virial coefficient on the hard-core agreed completely with the experiment. This trend is also true with $CH_4 + C_4H_{10}$ system. In the temperature range of parameter determination, the hard-core model gives better results than the Morse potential in the above cases. As for C_3H_8, it showed the largest deviation in the parameter determination for the hard-core model and from the trend of the systematic deviations in $CH_4 + C_3H_8$ system, the validity of the parameters for C_3H_8 is rather suspected.

It seems that the combining rules are satisfactory, but it is interesting that for one potential model, when better agreement is obtained by Eq. (23) than by Eq. (24), the same is true for other potentials. Even the empirical correlation of Huff and Reed[25] followed the same pattern. It appears that regardless of the functional form of the potential energy function, the energy of potential minimum for unlike interaction can be approximated from those for like interactions by the same combining rule. However, neither Eq.(23) nor Eq. (24) seems to present the unlike interaction properly. Actually, the dispersion attraction contains terms of higher order of inverse separation than 6. Eq. (23) which was derived on r^{-6} term only is not truly theoretical. To account for the unlike interaction properly, a more elaborate combining rule for the energy parameter should be developed.

It is felt that for more critical comparison of potentials, transport properties on the hard-core Morse potential should be calculated. Until that time the final comparison should be reserved.

CHAPTER III

ANGLE-AVERAGED PAIR-POTENTIAL ENERGY FUNCTION FOR
DILUTE POLAR GAS PROPERTIES

While there have been many pair-potential energy
models for spherical nonpolar molecules, the angle-dependent
12-6-3 Stockmayer potential is the only one that has been
used extensively for the interaction of a pair of polar
molecules. Rowlinson[26] demonstrated the successful
correlation of second virial coefficients of polar gases
with this potential. Saxena and Joshi[27] extended the
model by using 18-6-3 and 28-7-3 powers on the reciprocal
of the intermolecular separation. O'Connell and Prausnitz[28]
modified the Stockmayer potential by introducing the Kihara
hard-core model for the nonpolar part of the interaction
in place of the Lennard-Jones model. Monchick and Mason[29,30]
have applied the 12-6-3 Stockmayer potential to the correla-
tion of transport properties of dilute gases.

A potential energy function, which may be called the
12-6-6 model, for polar-polar and for polar-nonpolar pairs
contains the statistically weighted mean potential, averaged
over relative orientation, for the classical electrostatic
dipole-dipole and dipole-induced dipole interaction[31]
together with the Lennard-Jones 12-6 potential for the
contribution of the dispersion force interaction:

$$\langle\phi\rangle_{ij} = \varepsilon^{0}_{ij}\left[(r^{0}_{ij}/r)^{12} - 2(r^{0}_{ij}/r)^{6}\right] - \left[2\mu_{i}^{2}\mu_{j}^{2}\,\beta/3\right.$$

$$\left. + \mu_{i}^{2}\alpha_{j} + \mu_{j}^{2}\alpha_{i}\right]/r^{6} \qquad (29)$$

$\langle\phi\rangle_{ij}$ is the total weighted average mutual potential energy of the pair i, j. ε^{0}_{ij} and r^{0}_{ij} are empirical constants characteristic of the dispersion interaction of the molecular pair i and j, μ is dipole moment in zero external field, α is mean polarizability, and β is $(kT)^{-1}$. It is assumed in the derivation of the polar interaction term that molecules are point dipoles in the homogeneous field produced by the molecule at the other. The effective potential energy of the pair of molecules is approximated by the term in r^{-6} in the orientation-averaged electrostatic interaction.

$\langle\phi\rangle$ is thus an angle-independent potential but it is a function of temperature as required by the statistical averaging over the relative orientations.

The right-hand side of Eq. (29) may be arranged[31] into the usual 12-6 bireciprocal form,

$$\langle\phi\rangle_{ij} = \varepsilon^{*}_{ij}\left[\left(\frac{r^{*}_{ij}}{r}\right)^{12} - 2\left(\frac{r^{*}_{ij}}{r}\right)^{6}\right] \qquad (30)$$

where ε^{*}_{ij} and r^{*}_{ij} are functions of temperature,

$$\varepsilon^{*}{}_{ij} = \varepsilon^{0}{}_{ij} \left[1 + \mu_{i}^{2}\mu_{j}^{2}\ \beta/3r^{06}{}_{ij}\varepsilon^{0}{}_{ij} \right.$$

$$\left. + (\mu_{i}^{2}\alpha_{j} + \mu_{j}^{2}\alpha_{i})/2\ \varepsilon^{0}{}_{ij}r^{06}{}_{ij} \right]^{2} \tag{31}$$

and

$$r^{*}{}_{ij} = r^{0}{}_{ij}\ (\varepsilon^{0}{}_{ij}/\varepsilon^{*}{}_{ij})^{1/12} \tag{32}$$

This potential obviates the calculation of any additional
tables of reduced virial coefficients and collision integrals
for dilute gas properties since such tables already exist[22]
for the functional form of Eq. (30). In this model the
potential is averaged over all orientations before the
collision integral is calculated, whereas in the model of
Monchick and Mason[29] the collision integral is calculated
as a function of orientations and then averaged over all
orientations, giving equal weight to each orientation. In
both models it is assumed that there is no interchange of
rotational and translational energies during a collision.
The Stockmayer potential carries no terms for the dipole-
induced dipolar interaction that is included in the potential
of Eq. (29). $\langle\phi\rangle$ is a simple function and as shown here, is
as good as or better than the Stockmayer potential for
correlating, interpolating, and extrapolating dilute gas
data. It should be clearly understood here that the present
model is distinctly different from the 12-6 model in that
the averaged dipole-dipole and dipole-induced dipole
interactions are superposed to the latter to obtain the former.

For a single-component system $i = j$ always and the species subscripts may be deleted.

To calculate properties of a single-component gas the parameters ϵ^o and r^o as well as the dipole moment and the (mean) polarizability are required. The potential parameters are obtained by fitting the theoretical relationships to the experimental data. It is assumed that the dipole moment and polarizability are known molecular constants. The data used in the present calculations are those of gas viscosities treated by Monchick and Mason.[29]

The rigorous kinetic theory[33] gives the following expession for first order approximation to viscosity, η in gm./cm. sec., in a dilute gas:

$$\eta \times 10^7 = 266.92 \ \frac{(MT)^{1/2}}{\sigma^2 \ \Omega *^{(2,2)}} \tag{33}$$

where M is molecular weight, T is temperature in $^\circ K$, σ is the separation in $\overset{o}{A}$ at zero potential, and $\Omega *$ is the dimensionless collision integral. Here σ can be replaced by r^*, the separation at the potential minimum, using the relationship $2^{\frac{1}{6}} \sigma = r^*$ for the 12-6 potential. Since the experimental error is in the same order of magnitude as that of the correction term for higher theoretical approximations, the first approximation is adequate here. The two Eqs. (31) and (32) contain four unknowns, ϵ^*, r^*, ϵ^o, and r^o. Choosing two temperatures, T_1 and T_2, we obtain r_1^* and r_2^* in terms of ϵ_1^* and ϵ_2^*

from these relationships as:

$$r_1^{*6} = \frac{1}{3} \frac{\mu^4}{\varepsilon_1^* - (\varepsilon_1^* \varepsilon_2^*)^{\frac{1}{2}}} (\beta_1 - \beta_2) \tag{3}$$

where the subscripts 1 and 2 now refer to the temperatures. The same relationship for r_2^{*6} can be obtained by interchange of subscripts 1 and 2. The r^*'s are eliminated from these equations by introducing the theoretical expression from Eq. (33) for each temperature. The resulting expressions rearranged give the working equations:

$$\varepsilon_1^* \varepsilon_2^* = (\varepsilon_1^* - A_1)^2 \tag{35}$$

$$\varepsilon_1^* \varepsilon_2^* = (\varepsilon_2^* - A_2)^2 \tag{36}$$

where

$$A_1 = \frac{8.7631 \times 10^{-12} \mu^4 \Omega_1^{*3} \eta_1^3}{(MT_1)^{3/2}} (\beta_1 - \beta_2) \tag{37}$$

and similarly for A_2.

When viscosities at T_1 and T_2 are known then ε_1^* and ε_2^* are the only explicit unknowns in Eqs. (35) and (36). The values of ε_1^* and ε_2^*, which satisfy these two are the energy parameters at T_1 and T_2. r_1^* and r_2^* are then evaluated by Eq. (34).

The temperature-independent parameters, r^0 and ε^0, are obtained in terms of r^* and ε^* from Eqs. (31) and (32) as:

$$r^{06} = \left[1 - \frac{\mu^4 \beta}{\varepsilon^* r^{*6}} - \frac{\mu^2 \alpha}{\varepsilon^* r^{*6}} \right]^{-1} r^{*6} \tag{35}$$

$$\varepsilon^{O} = \varepsilon^*(r^*/r^O)^{12} \tag{39}$$

In this way ε^O can be computed from two experimental viscosities.

The potential parameters for several polar gases determined by this method are given in Table 5, along with molecular constants μ and α , and references for viscosity data. Dipole moments are taken from Monchick and Mason[29] and polarizabilities are taken from Landolt-Börnstein Tables.[34]

Eqs. (35) and (36) each gave curves for ε_1^* vs. ε_2^* of small curvatures and a small portion of each curve was approximated by a straight line. A graphical method was used to find ε_1^* and ε_2^* in this work. In all cases, except HBr for which there are only two viscosities, the intersection of the two curves could be easily and accurately located. For water vapor ε^* is very large at low temperatures ($\varepsilon^*/k = 2280°K$ at $273°K$). To be able to use the 12-6 tables for water vapor, the high temperature data of Bonilla, Wang and Weiner's smoothed data[35] were used without any correction mentioned by others.[29]

The experimental and calculated gas viscosities at one atmosphere pressure are compared in Figures 1,2 and 3. The data points used in the determination of the parameters are marked by crosses. Arbitrarily chosen data points are reproduced in the figures. The curves are calculated values. For most of the molecules considered the agreement is within the experimental error. The deviation in H_2O is the largest
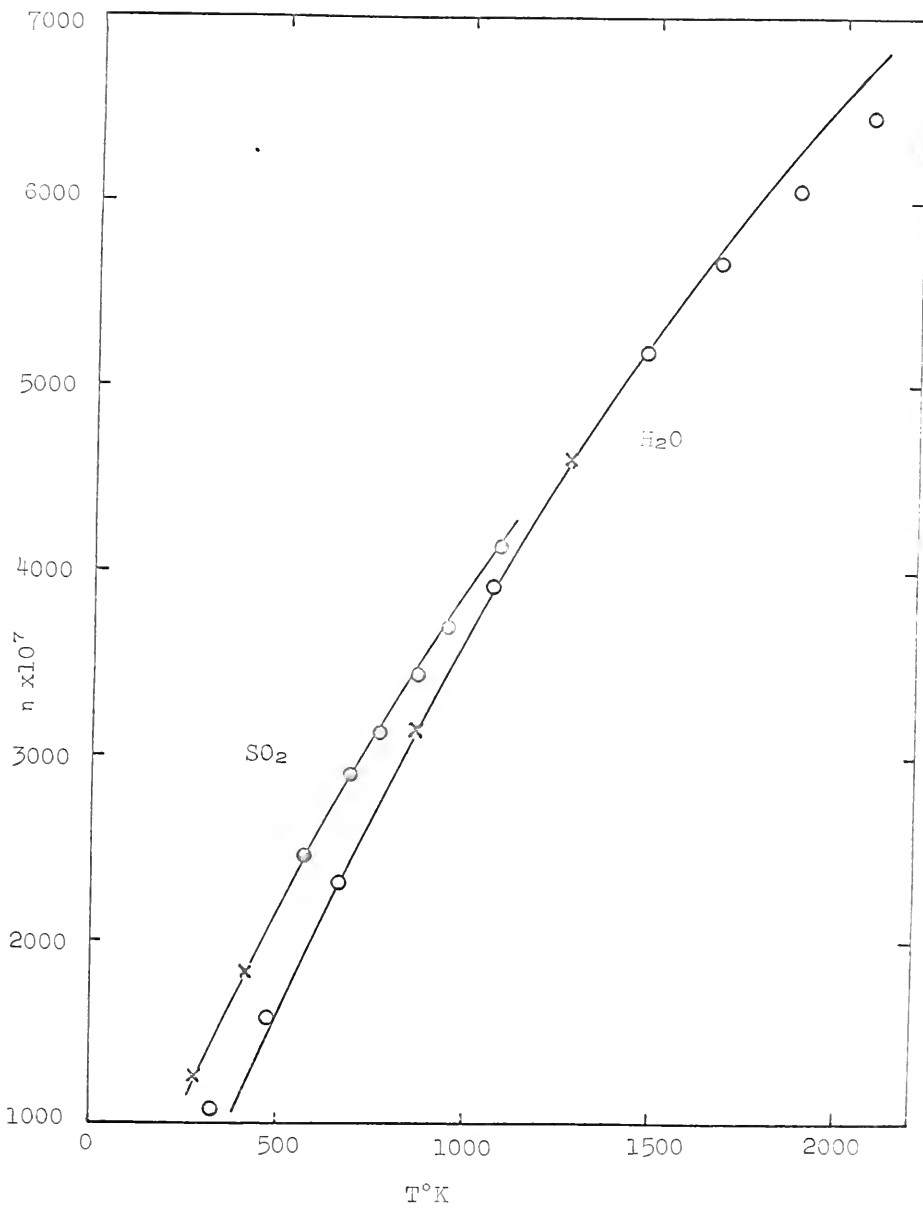
Figure 1   Viscosities for H_2O and SO_2
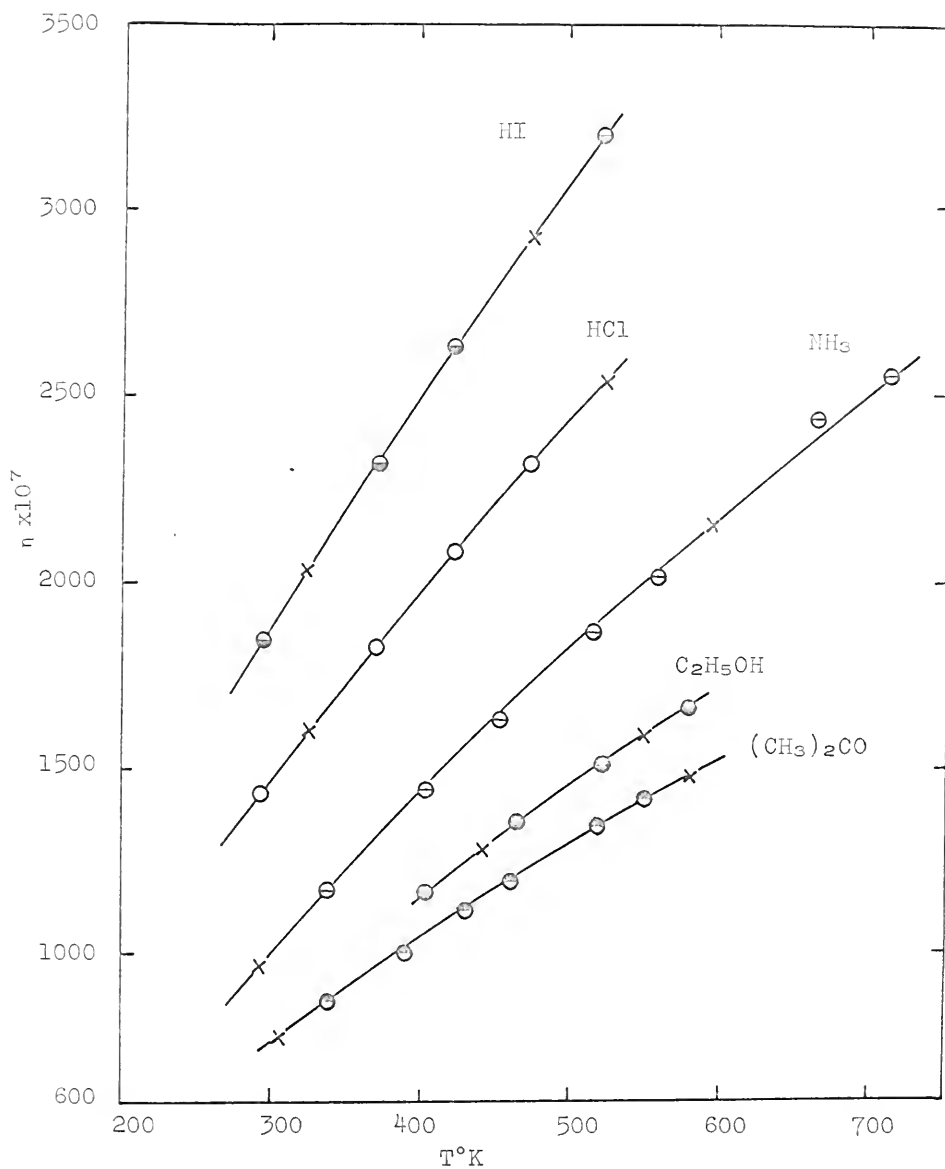
Figure 2   Viscosities for HI, HCl, NH₃, C₂H₅OH and (CH₃)₂CO
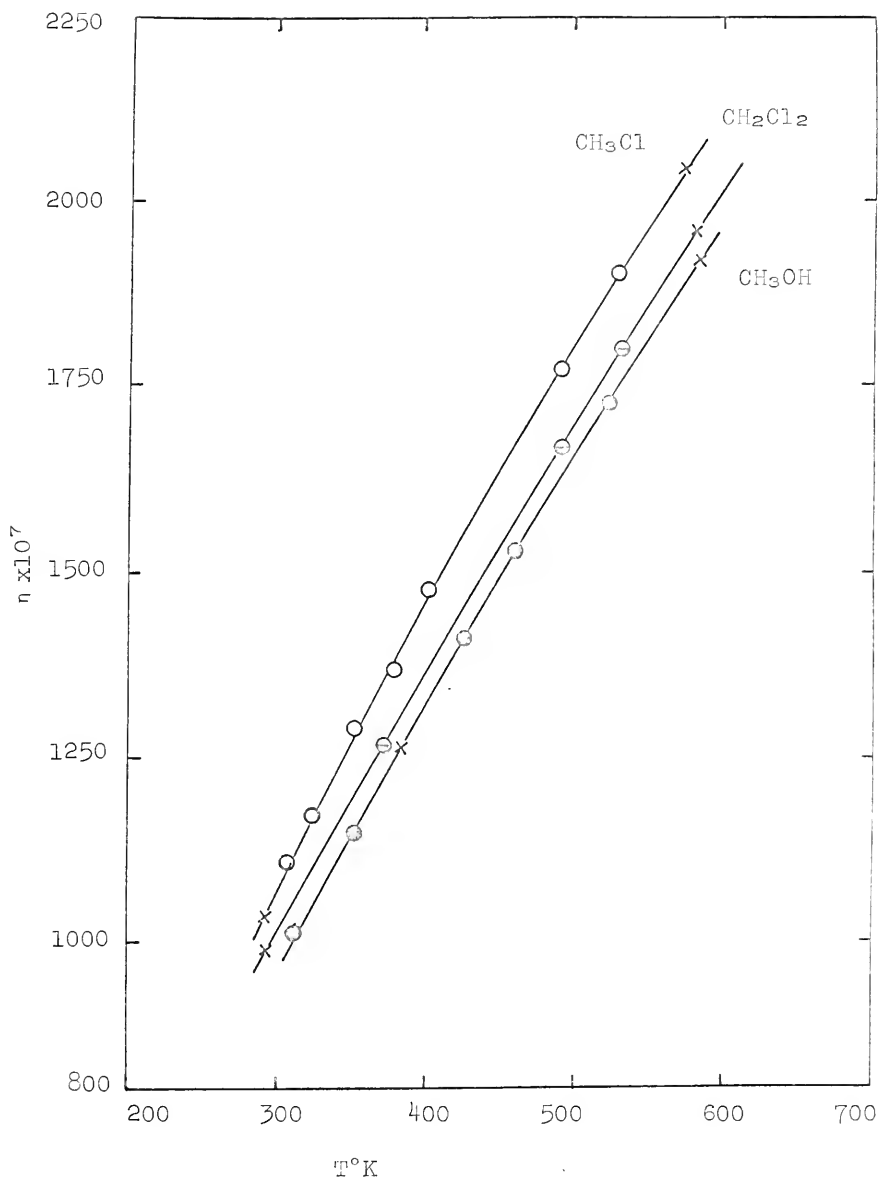
Figure 3   Viscosities for CH₃Cl, CH₂Cl₂ and CH₃OH

among all the molecules studied. At the extreme high temperature of 2073°K the deviation is +3.8%. For the remaining molecules the agreement seems to be as good as those obtained for nonpolar gases with the usual potentials.[32]

The method of determining parameters from experimental data is straight-forward. It does not suffer from the subjectivity frequently characteristic of graphical methods. Theoretically ε * and r* should be constant at a given temperature. We paired one temperature with several others and calculated ε* and r* at the fixed temperature from the several different combinations. The values found differed less than 1% from one another.

The temperature-dependent factors in Eqs. (31) and (32) are monotonously decreasing and increasing respectively. The temperature dependence is rather small for r* and large for ε*, especially when the molecule has large dipole moment. For the feebly polar molecules, like HI and $CHCl_3$, ε */ ε^0 is near unity while for strongly polar molecules, like H_2O, NH_3, and $(CH_3)_2CO$, ε*/ ε^0 is large; e.g., for H_2O ε */ ε^0 = 11.4 at 273°K.

The second virial coefficient, computed with $<\phi>$ and the 12-6 tables and the parameters of Table 5, are shown in Table 6. The second virial coefficient data for SO_2 are taken from Kang et al.[36] and all others from Rowlinson.[26] The agreement between observed and calculated values are as good or as poor as those obtained by Monchick and Mason[29] with the angle-dependent potential and viscosity parameters.

No potential has been found which is successful with a single
set of parameters for a given molecular pair for both
equilibrium and transport properties of polar molecules.

Usually the transport properties are better predicted
with the parameters determined from other transport properties.
For the polar molecules under consideration the only available
experimental value is the self-diffusion coefficient of HCl.
Theoretically the self-diffusion coefficient, D in cm.^{2}/sec.,
in the first approximation is written as:

$$D = 0.002628 \ \frac{(T^3/M)^{1/2}}{P \ \sigma^2 \ \Omega^{*(1,1)}} \tag{40}$$

where P is the pressure in atmosphere and other symbols
have the same meaning as before. By use of this formula,
the self-diffusion coefficient of HCl at 295°K was computed
to be 0.1261 from 12-6 tables and the parameters of Table 5.
If we take Braune and Zehle's[37] value of 0.1254 (as
corrected for the mass of isotopic tracers by Monchick
and Mason) the deviation is + 0.56 % which is well within
the experimental error.

The parameters, ε^o and r^o, hypothetically are those
for the dispersion part of the total intermolecular interaction.
The theory of Mavroyannis and Stephen[24] for interaction
between atoms gives an expression for the interaction constant
$\varepsilon^o r^{o6}$ in terms of the polarizability, α, and the total
number of electrons, Z, in the molecule as:

$$\varepsilon^{\,0} r^{\,0^6} = 6.292 \times 10^{-12} \; \alpha^{\,3/2} \, Z^{1/2} \quad \text{erg} \times \overset{\circ}{A}{}^6 \tag{41}$$

when 12 is used as the repulsion-term exponent. The negative of four times $\varepsilon^{\,0} r^{\,0^6}$ is the coefficient on r^{-6} in the dispersion energy interaction. This theoretical value for $\varepsilon^{\,0} r^{\,0^6}$ is compared in Table 7 with the corresponding empirical value calculated with the parameters of Table 5. The agreement is rather close for the smaller polar molecules and becomes poor for the larger polyatomic ones.

The agreement between the Mavroyannis-Stephen theory and data for nonpolar molecules is illustrated in the lower part of Table 7. The agreement is very good for the monatomic and diatomic molecules and becomes poor as the number of atoms per molecules increases.

The parameters $\varepsilon^{\,0}$ and $r^{\,0}$ for the polar molecules thus appear to fulfill their role as representative of the dispersion part of the total interaction in a manner which is as realistic as the parameters for the toal interaction between two nonpolar molecules in the 12-6 form. It is interesting to find that the Mavroyannis-Stephen expression for dispersion interaction so accurately confirms the experimental interaction constant $\varepsilon^{\,0} r^{\,0^6}$ for small molecules, both polar and nonpolar. The London formulas, on the other hand, predict values of $\varepsilon^{\,0} r^{\,0^6}$ that are low by a factor of 1.6 for monatomic molecules and still worse for diatomic and larger molecules.[24]

CHAPTER IV

TRANSPORT PROPERTIES OF POLAR-NONPOLAR GAS MIXTURES

The angle-averaged potential energy function of Chapter III is applied to binary mixtures containing polar gases, specifically to polar-nonpolar mixtures since no data exist for polar-polar mixtures.

The unlike-pair interactions may be approximated from those for like-pairs. It is clear from Eq. (31) that ε^{*}_{ij} cannot be a geometric mean of ε^{*}_{ii} and ε^{*}_{jj}. The dispersion force parameter ε^{o}_{ij} is expected to be close to geometric mean of ε^{o}_{ii} and ε^{o}_{jj} and the arithmetic mean rule is used for r^{o}_{ij}.

$$\varepsilon^{o}_{ij} = (\varepsilon^{o}_{ii} \varepsilon^{o}_{jj})^{1/2} \qquad (42)$$

$$r^{o}_{ij} = (r^{o}_{ii} + r^{o}_{jj})/2 \qquad (43)$$

Using dipole moments and polarizabilities, ε^{*}_{ij} and r^{*}_{ij} can be calculated by Eqs. (31) and (32).

When one member of the pair is nonpolar, ε^{*}_{ij} and r^{*}_{ij} are no longer temperature-dependent since the term in $\mu^{2}_{i} \mu^{2}_{j}$ is then zero. Nevertheless, ε^{*}_{ij} is not a geometric mean since the dipole-induced dipole interaction is included

in the potential. Usually the induced moment is ten times smaller than the inducing one and the model is almost the same as the 12-6 potential. However, this should be more realistic than the 12-6 model and as shown here the parameters for the 12-6-6 model successfully predict the properties of polar-nonpolar mixtures.

Making use of the combining rules in Eqs. (42) and (43) and the empirical values, previously obtained from gas viscosities, of ε^o and r^o in like-pair interactions, the viscosity, diffusion coefficient, and thermal diffusion factor were calculated and compared with experimental properties for the binary systems in Tables 9, 10, and Figures 4,5, and 6. The potential parameters for nonpolar gases used in the calculation are given in Table 8 along with polarizabilities. Thermal conductivity is not considered here because of its dependence on the internal energy transfer.

From the kinetic theory the expression for the viscosity of binary mixture can be written as:

$$\eta_m = \frac{1 + Z}{X + Y} \tag{44}$$

where X, Y, and Z are functions of mole fraction, molecular weight of the component, and the collision integrals for the unlike-interaction. Expressions for X, Y, and Z have been given elsewhere.[32]

In Table 9 the calculated viscosities and the deviations from experimental data are presented. The average deviation of calculated values from experiment is about

1.3% which favorably compares with the results of Mason
and Monchick.[30] The agreement is within experimental error
and not worse than those of the 12-6 potential[32] or modified
Buckingham model[38,39] for nonpolar spherical molecules.

The diffusion coefficient of binary mixtures, D_{12},
is calculated by:[32]

$$D_{12} = \frac{0.002628 \ (T_3/2m)^{1/2}}{P \ \sigma_{12}^2 \ \Omega_{12}^* \ (1,1)} \tag{45}$$

where m is reduced molecular weight, P the pressure in
atmosphere, T in °K, and σ the separation at zero potential
in $\overset{\circ}{A}$. The calculated values are compared with experiment in
Table 10. The average deviation of calculated values from
experimental data is about 5.5% which again confirms that
this model is as good as either the 12-6 potential or the
modified Buckingham model for nonpolar molecules.

It is interesting to compare the parameters for
$H_2O + O_2$ system with those obtained by others. The values
by Eqs. (31) and (32) are $\sigma_{12} = 3.49 \ \overset{\circ}{A}$ and $\varepsilon_{12}^*/k = 167.7°K$
which lie between Mason and Monchick's[30] ($\sigma_{12} = 3.072 \ \overset{\circ}{A}$,
$\varepsilon_{12}^*/k = 239°K$) for the Stockmayer potential and Walker and
Westenberg 's [40] ($\sigma_{12} = 3.335 \ \overset{\circ}{A}$, $\varepsilon_{12}/k = 80°K$) for the
12-6 potential. The systems involving H_2O as one component
show improved agreement with experimental over Mason and
Monchick's results.

The thermal diffusion factor is a complex function of temperature, concentration, and molecular interaction. It is hard to predict this property theoretically. Two approximations are those of Chapman-Cowling[33] and Kihara-Mason.[8,41] Kihara's first approximation was used because of its simplicity. This is known to give more accurate results than Chapman-Cowling's first approximation and differs from the second approximation by a few percent. In Kihara's first approximation, the thermal diffusion factor, α_T, is written as:

$$\alpha_T = (6C_{12}* - 5) \frac{x_1 S_1 - x_2 S_2}{x_1^2 \, Q_1 + x_2^2 \, Q_2 + x_1 x_2 \, Q_{12}} \tag{46}$$

where x is mole fraction of the component. Expressions for S_1, S_2, Q_1, Q_2 and Q_{12} have been given by Mason[42] but they are omitted here because of their length. $C_{12}*$ is the ratio of collision integrals, $\Omega*^{(1,2)}$ over $\Omega*^{(1,1)}$, for the unlike-interaction.

The experimental data for the systems $H_2O + H_2$,[43] $SO_2 + H_2$,[44] $Ar + HCl$,[45] and $Ne + NH_3$[46] are compared with calculated values in Figures 4, 5, and 6. Curves refer to the calculated values and circles refer to the experimental values. In Figure 4 open circles and curve 1 refer to values at 566°K and solid circles and curve 2 to those at 368°K. In Figure 6 curve 1 and open circles refer to the values for $Ar + HCl$. The temperature for $SO_2 + H_2$ is 376°K and that
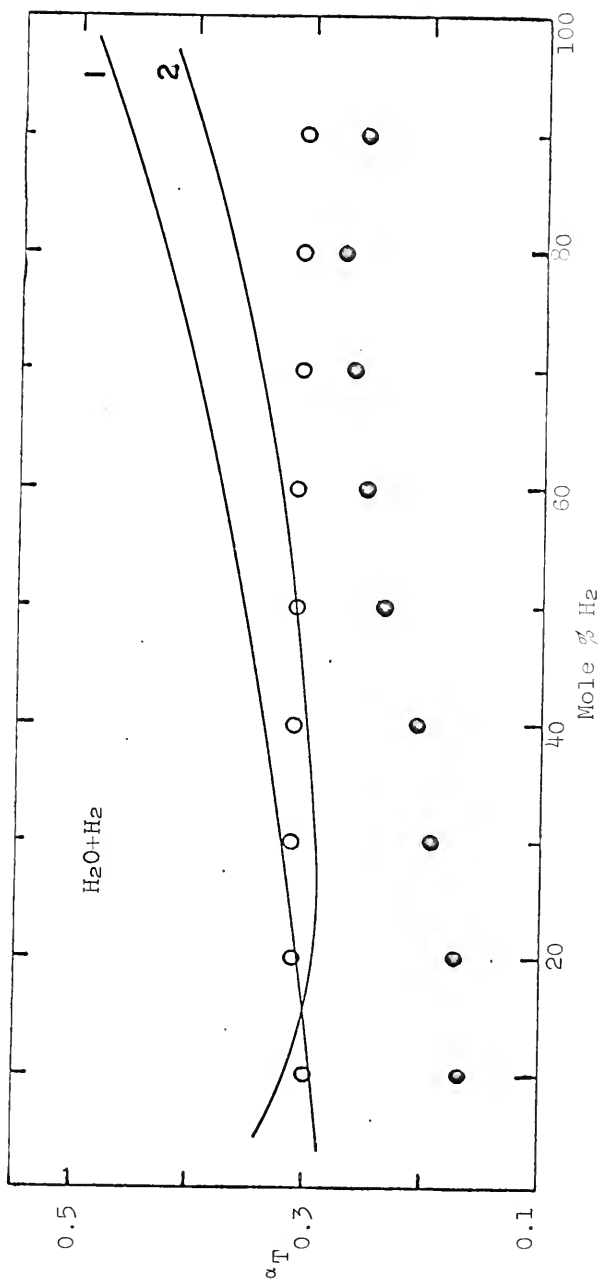
Figure 4   Thermal Diffusion Factors for H₂O:H₂ System
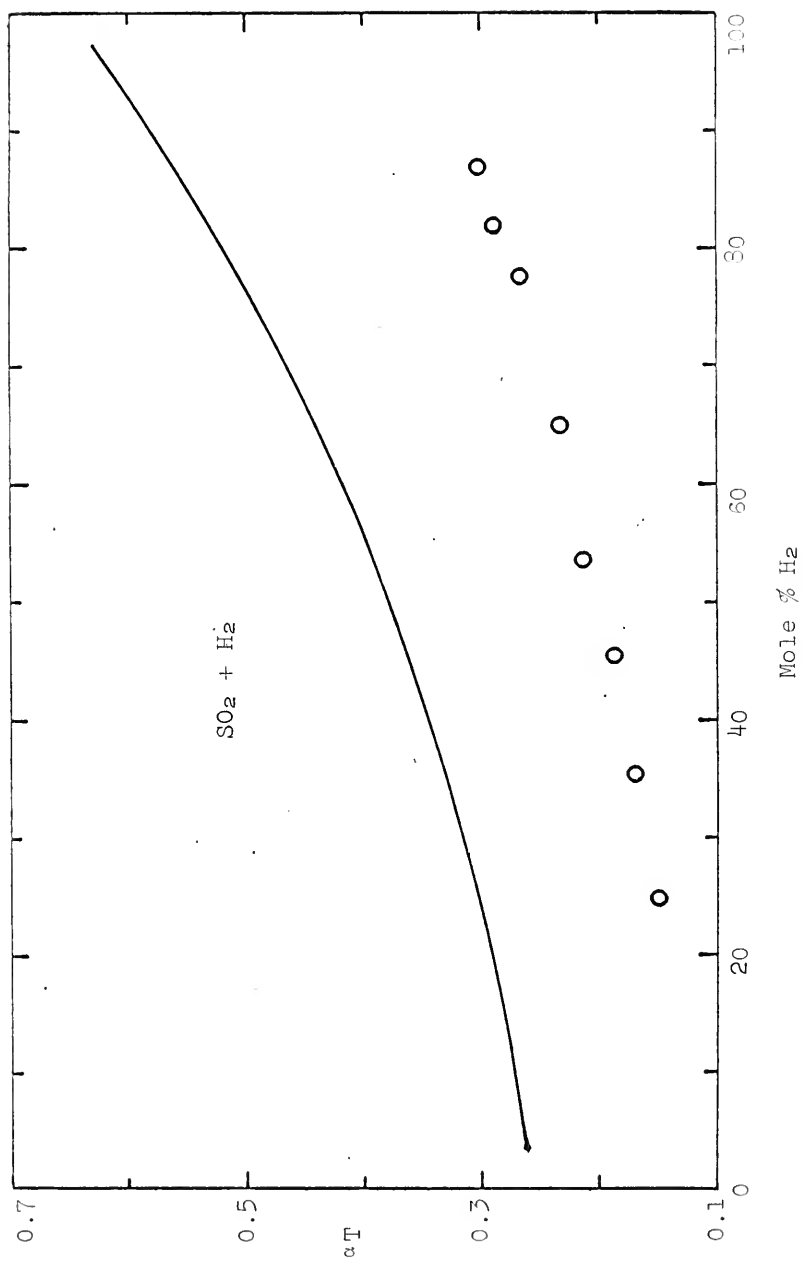
Figure 5   Thermal Diffusion Factors for SO₂ + H₂ System
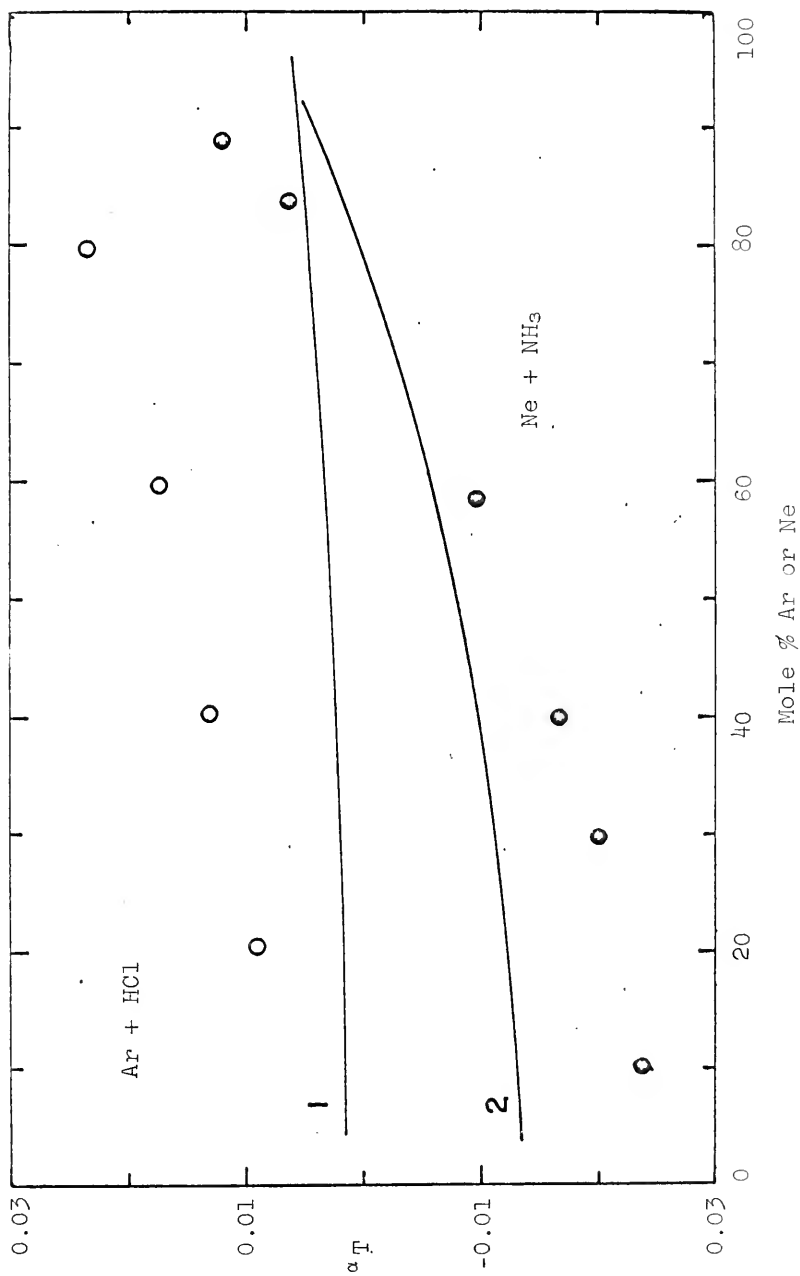
Figure 6   Thermal Diffusion Factors for Ar+HCl and Ne+NH₃ Systems

for Ar + HCl and Ne + NH$_3$ is $383°K$. The overall agreement

is fair and compares with other calculations for polar gases.

For the H$_2$O + H$_2$ system the data of Whalley seem too uncertain

with the trend of the calculated values. However, the

Ne + NH$_3$ system shows a good agreement and the inversion

point is correctly predicted as shown in Figure 6.

It can be said from the results that the 12-6-6

potential can be used for polar gas mixtures with success.

The 12-6-6 model gives correlation at least as good as,

or better than the more elaborate model of Monchick and

Mason for mixtures containing polar gases. When comparing

the result on viscosities of binary mixtures between these

two models, one should bear in mind that Monchick and Mason

used the experimental data for pure components to force

the calculated values to fit at both ends of the composition

range. When the calculated viscosity was used for one

component in H$_2$ + (C$_2$H$_5$)$_2$O system the deviation was the

largest among all the systems used in their calculation.

In the case of those systems containing NH$_3$ as one

component, the deviation is the largest at the polar end

of composition. This arises from the fact that when the

parameters for NH$_3$ were obtained from the viscosities at

two different temperatures, the deviations at other tempera-

tures were rather large. Thus, at low temperatures near

those used in the fit, this trend disappears.

As the agreement is not very good for the thermal diffusion factor which is the most sensitive to the unlike-interaction, it is suggested that the combining rules can be refined to give better agreement between experiment and calculation. However, the agreement in the diffusion and viscosity does not warrant any further complications in the combining rules.

CHAPTER V

SECOND VIRIAL AND JOULE-THOMSON
COEFFICIENTS OF POLAR GASES

In Chapter III the parameters for the angle-averaged
potential model were determined from the experimental
viscosities of polar gases. The calculations of transport
properties with these parameters were very successful but
those of second virial coefficients were not impressive.
In this chapter the parameters are determined from the
existing second virial coefficients of polar gases. The
validity of the parameters are further tested by computing
the Joule-Thomson coefficients at zero pressure for several
molecules for which experimental data are available.

To determine the parameters, ε^{o} and r^{o}, from the
second virial coefficients, a similar method to that of
Chapter III is chosen. For the 12-6 potential the second
virial coefficient is given by:

$$B(T) = \frac{2^{\frac{1}{2}}}{3} \pi N r^{*3} B* \qquad (47)$$

where the symbols have the same meaning as before and values
of B* have been tabulated elsewhere.[32] We choose two
temperatures, T_1 and T_2, and the corresponding values of

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B(T), B_1 and B_2, where subscripts 1 and 2 refer to the temperatures. Eliminating r*'s from these equations by the use of Eq. (34) the working equations of Eqs. (35) and (36) are obtained with:

$$A_1 = 1.3916 \times 10^{+7} \ \frac{\mu^4 (B_1^*)^2}{B_1^2} \ (\beta_1 - \beta_2) \qquad (43)$$

and similarly for A_2. The symbols are in the same unit as before. With two known B_1 and B_2 at T_1 and T_2, the values of ε_1^* and ε_2^* and consequently those of r_1^* and r_2^* can be evaluated. Then by Eqs. (38) and (39) ε^o and r^o can be computed.

The potential parameters for several polar gases determined by this method are given in Table 11. Values of dipole moment and polarizability in Chapter III are used except the following.

	μ , debye	α , $\mathring{A}^3$
CH_3CN	3.44	4.47
CH_3CHO	2.68	4.43
C_2H_5Cl	2.05	6.4

The value of α for CH_3CN is taken from Moelwyn-Hughes[47] and α for CH_3CHO is calculated from the bond polarizabilities. All other values are given in Landolt-Börnstein Tables. The experimental second virial coefficients of SO_2 are taken from Kang, et al.[36] and others from Rowlinson.[26] The values of ε_1^* and ε_2^* are found graphically. However,

they could not be located for CH_3OH and CH_3Cl for which the curves by Eqs. (35) and (36) ran parallel.

The Joule-Thomson coefficient is defined as the rate of change of temperature with pressure in an isenthalpic expansion. This property is related to the equation of state by:

$$\bar{\mu} = \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] / C_p \qquad (49)$$

where $\bar{\mu}$ is the Joule-Thomson coefficient, V is the volume, and C_p is the heat capacity of the gas. This equation can be expanded by the use of the virial equation of state and in the limiting case of $p = o$, the Joule-Thomson coefficient at zero pressure, $\bar{\mu}^{\,o}$, is obtained as follows:

$$\bar{\mu}^{\,o} = \frac{1}{C_p^{\,o}} \left(T \frac{dB}{dT} - B \right) \qquad (50)$$

where $C_p^{\,o}$ is the molar heat capacity at zero pressure and at that particular temperature under consideration. Since the potential parameters are temperature-dependent we have:

$$T \frac{dB}{dT} - B = b_o \left(T^* \frac{dB^*}{dT^*} - B^* \right) + TB^* \frac{db_o}{dT} - b_o \frac{T^{*2}}{k} \frac{dB^*}{dT^*} \frac{d\epsilon^*}{dT} \qquad (51)$$

where b_o is $(2/3)\,\pi N\,\sigma^3$ and other reduced variables are defined earlier. Eqs. (31), (32), and (51) combined with (50) give the Joule-Thomson coefficient at zero pressure for the present model.

$$\bar{\mu}^{\,\circ} = \frac{1}{C_p^{\,\circ}} \left[b_0 \left(T^* \frac{dB^*}{dT^*} - B^* \right) + \frac{b_0\, \mu^4}{(\varepsilon^*)^2 r^{\circ 6}} \left(\frac{\varepsilon^*}{\varepsilon^{\,\circ}} \right)^{\frac{1}{2}} \right.$$

$$\left. X \left(\frac{B^*}{6T^*} + \frac{2}{3} \frac{dB^*}{dT^*} \right) \right] \tag{52}$$

When molecules are nonpolar, only the first term of Eq. (52) remains which is the Joule-Thomson coefficient of nonpolar molecules. By the knowledge of either the second virial coefficient and its derivative with respect to temperature or the potential parameters, the Joule-Thomson coefficient at zero pressure can be easily calculated. Tables of $T^* \frac{dB^*}{dT^*}$ have been computed for the 12-6 potential.[32]

The Joule-Thomson coefficients at zero pressure calculated by using the parameters determined from the second virial coefficients are compared with the experiment in Table 12. The experimental data are taken from Diaz-Pena.[48] The heat capacities at zero pressure for SO_2 and H_2O are taken from Hougen, et al.[49] and those of NH_3 from Osborne, et al.[50]

The experimental and calculated second virial coefficients are compared in Figures 7, 8 and 9 where the curves are calculated values. The data points used in the determination of the parameters are marked by crosses. For most of the molecules considered the agreement is within experimental error. For NH_3, SO_2 and H_2O the agreement is extremely good but for CH_3Cl and $(CH_3)_2CO$ the curvature of calculated curves seems a little larger than that of experiment.
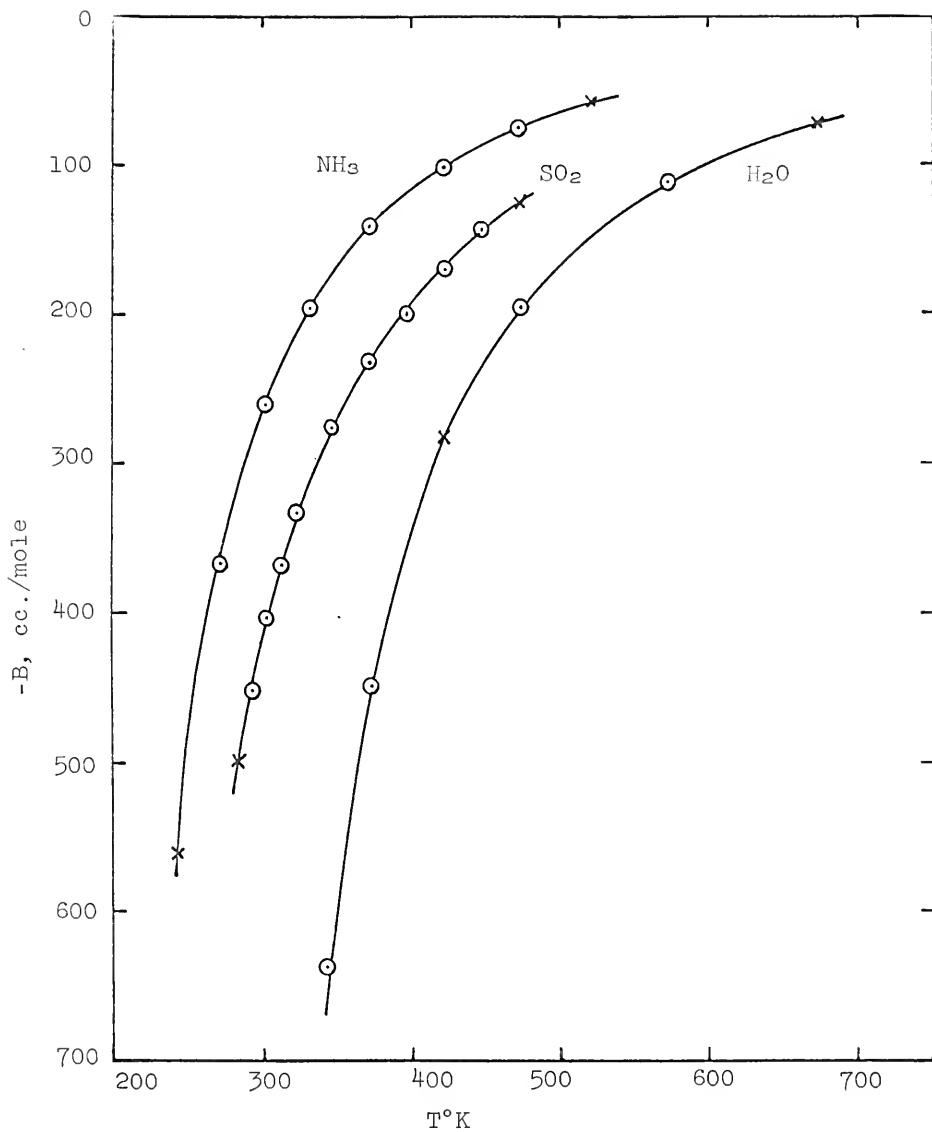
Figure 7   Second Virial Coefficients for
            NH_3, SO_2 and H_2O
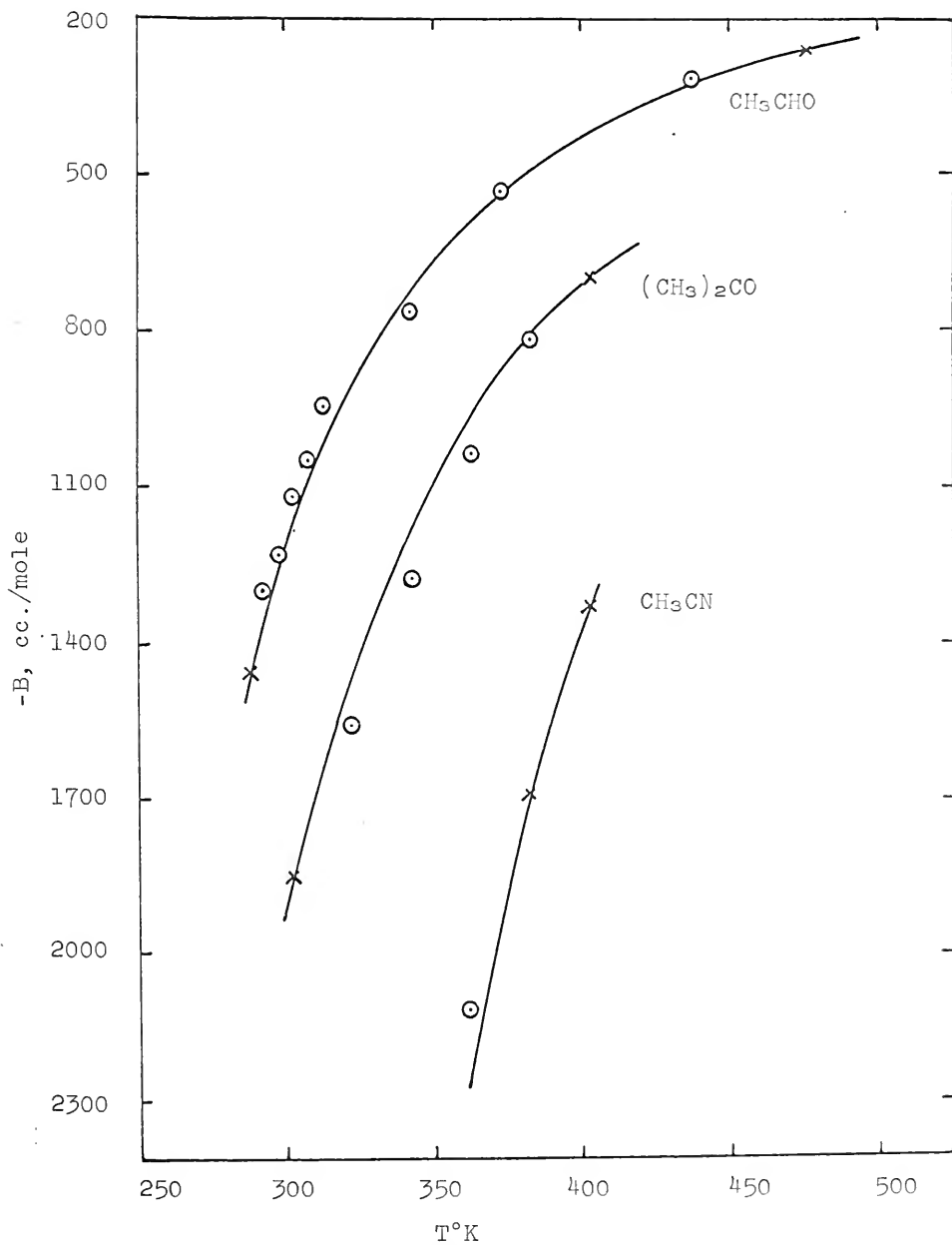
Figure 8   Second Virial Coefficients For
CH₃CHO, (CH₃)₂CO and CH₃CN
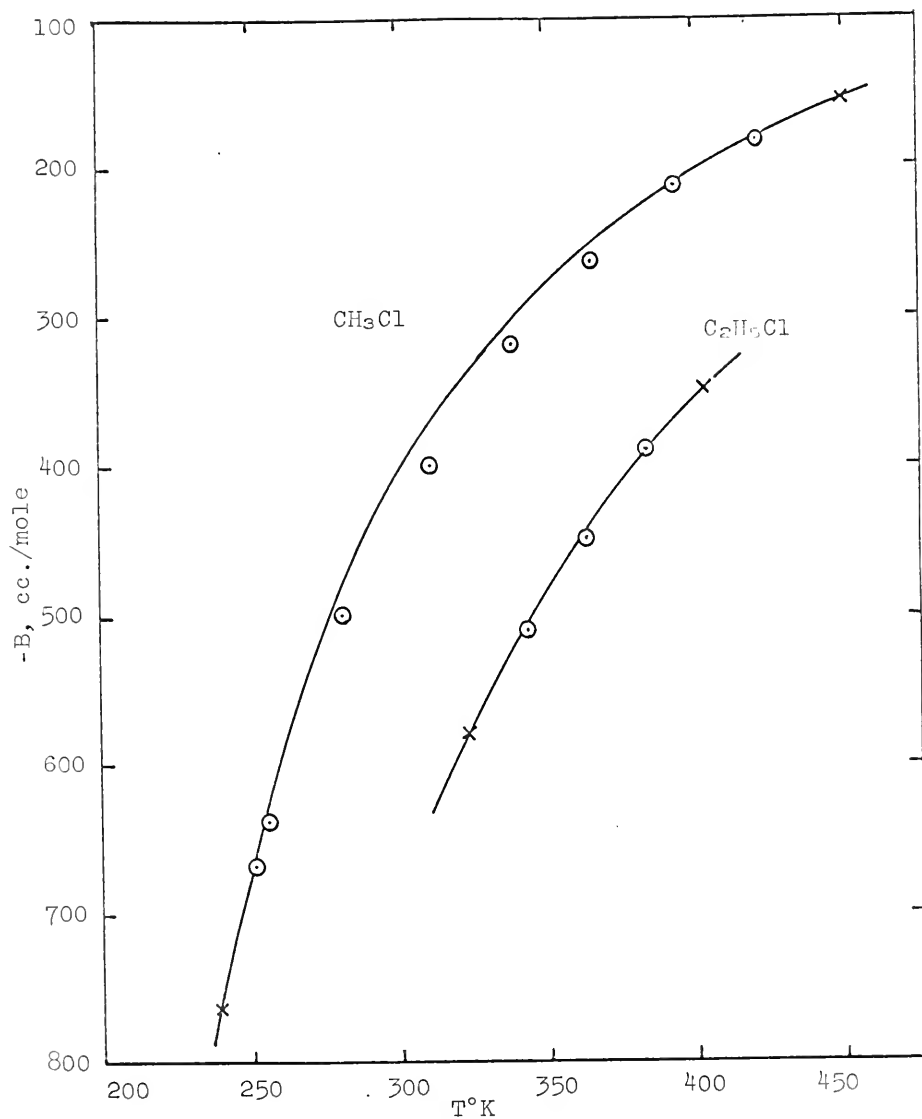
Figure 9   Second Virial Coefficients for CH₃Cl and C₂H₅Cl

The values of ε^{o}/k obtained from the second virial coefficients are always larger than those from viscosities. As can be expected r^{o} values are smaller than those of Chapter III except H_2O for which both ε^{o}/k and r^{o} are larger than those obtained from viscosities. In Table 11 the ratios of empirical to theoretical dispersion interaction constant are also given. The theoretical values are computed by the theory of Mavroyannis and Stephen of Eq. (41). It is interesting to note that except for H_2O the ratios are smaller than those of Chapter III. This trend is contrary to the expectation based on the fact that the integrals of the second virial coefficient and transport property place emphasis on the attractive and repulsive section of the potential, respectively. However, the parameters are consistent compared with those for the Stockmayer potential.[26] In the latter case σ for CH_3Cl and CH_2Cl_2 are smaller than that for CH_4 which is most unlikely.

The mean deviation in the calculations of the Joule-Thomson coefficient at zero pressure is 10.8%. For H_2O, NH_3, and SO_2 the deviations are 3.3, 16.4 and 16.8%, respectively, which seems quite satisfactory. The contribution of the second term in Eq. (52) ranged from about 10% up to about 40% in this calculation. The agreement for H_2O is excellent but for NH_3 and SO_2 the deviation seems rather systematic. The second virial coefficient and heat capacity are reproduced within 0.5% with the correlations used for these molecules. In this respect the deviations

in the Joule-Thomson coefficient are unreasonable. It
may be possible that the experimental data, either $\bar{v}$ or
B or both, are in error. At least they are not completely
consistent.

The angle-averaged potential is as good for polar
molecules as the 12-6 model for nonpolar molecules. It
can reproduce both thermodynamic and transport properties
of gases within experimental error. Unfortunately, it
apparently fails to correlate both properties with a single
set of parameters.

CHAPTER VI

ESTIMATION OF 12-6-6 POTENTIAL ENERGY FUNCTION
PARAMETERS FROM CRITICAL TEMPERATURES
AND POLARIZABILITIES

In the preceding chapters the angle-averaged pair-
potential energy function has been investigated to correlate
properties of polar gases. The model with temperature-
dependent parameters proved to be successful. The potential
parameters are determined from experimental viscosities
and second virial coefficients and this is usually the case
with other potentials. However, for any potential model
to be truly useful in predicting properties of materials,
there must be a method of estimating the parameters with
confidence from some simple, easily accessable properties.
In fact, for the Lennard-Jones 12-6 potential there have
been several methods of estimating the parameters, i.e.,
from critical constant,[32] from polarizabilities,[51] and
from saturated liquid densities at low pressure.[52]   In
this chapter the angle-averaged potential parameters are
estimated from critical temperatures and polarizabilities.

The principle of corresponding states has been used
to predict the potential parameters for 12-6 potential
model.[32]   This principle is based on several assumptions,[53,54]

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among which the following are important to the present
discussion; (1) the molecules are spherically symmetrical,
(2) the potential energy is only a function of intermolecular
separation. Thus, with the 12-6 potential model which is
good for simple, spherically symmetrical molecules, large
molecules show deviations from the corresponding states
theorem and should be treated differently.[55,56] As for
the polar molecules, the above assumptions cannot be true.
The present model, Eq. (29), was rather successful with
polyatomic, nonspherical molecules as was shown in earlier
chapters. Moreover, the potential energy is only a function
of intermolecular separation in the form of Eq. (30) although
it is also an implicit function of temperature, dipole
moments, and polarizabilities. Eq. (30) also satisfies the
requirement of universal functional form for the potential
energy. Therefore, we can follow the derivation[53,54] of
the principle of corresponding states. Indeed the dependence
of the parameters on those properties does not hinder the
integration over momenta in the partition function. From
the conditions for the critical states it follows that at
the critical state, kT_c/ε^*_c and $V_c/r^*_c{}^3$ should be universal
constants. Here we used the subscript c to denote critical
values.

For the present purpose of estimating ε^o and r^o only
ε^*_c need be known. Using the parameters in Chapter III,
values of ε^*_c/kT_c are calculated and given in Table 13
along with critical temperatures. In view of the nature of

water it was taken out in the average. It was thus obtained the relationship,

$$\varepsilon^{*}_{c}/k = 0.727 \ T_{c} \tag{53}$$

The calculated values of ε^{*}_{c}/k by Eq. (53) are compared with experiments also in Table 13. The average deviation is about 16%. Since all the molecules are large and nonsymmetrical the deviation seems not so bad.

The theory of Mavroyannis and Stephen for the dispersion attraction is given in Eq. (41). This theory is in the same functional form as that of Slater-Kirkwood[57] but it uses the total number of electrons in the atom rather than the uncertain number of valence electron in the latter theory. It was shown in Chapter III that the deviation of the calculated values of $\varepsilon^{o}r^{o6}$ from the empirical values becomes large for large molecules. Eq. (41) suggests that when $\varepsilon^{o}r^{o6}$ is plotted against $\alpha^{3}Z$ on a full logarithmic scale, it should yield a straight line of slope 0.5. In Figure 10 this kind of plot was made. For the polar molecules all the information is taken from the preceding chapters. The broken line, calculated by Eq. (41), does not satisfy those empirical points. By the method of least squares an empirical equation is obtained for the molecules considered here.

$$\varepsilon^{o}r^{o6} = 4.968 \times 10^{-12} \ (\ \alpha^{3}Z)^{0.5985} \ \text{erg} \ \overset{o}{\text{A}}^{6} \tag{54}$$

The empirical line is also shown in Figure 10.
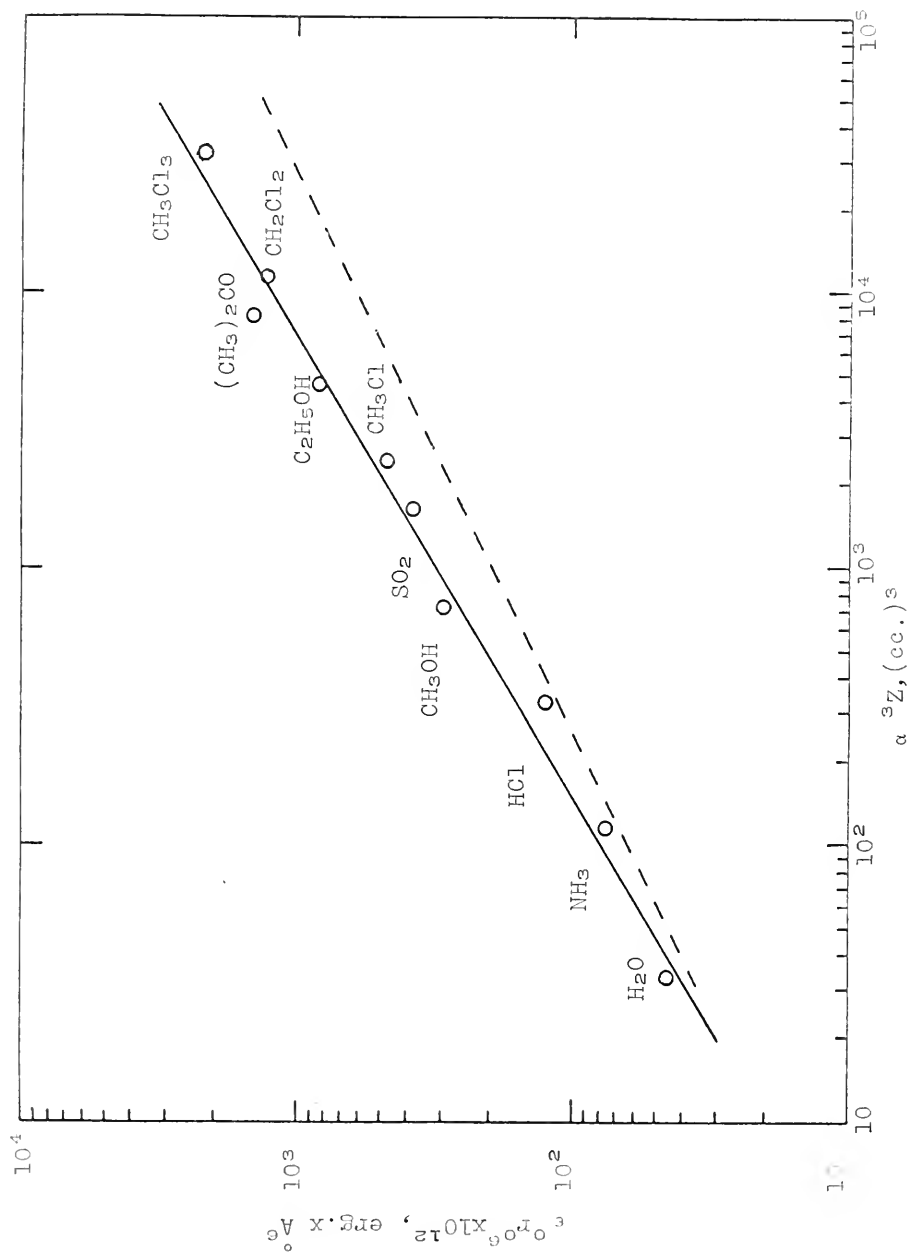
Figure 10   Dispersion Attraction Constants for Polar Gases

The parameters, ε^o and r^o, can now be estimated. From Eqs. (53) and (54) $*_c/k$ and $\varepsilon^o r^{o6}$ can be calculated. Then by Eq. (31) ε^o/k can be evaluated with known dipole moment and polarizability. The value of r^o follows directly from the value of $\varepsilon^o r^{o6}$. In this way the values of ε^o and r^o are calculated and compared with empirical values in Table 14. The average deviations of the calculated values of ε^o/k and r^o are 14.0% and 5.7%, respectively, which seem quite satisfactory and compare favorably with those of 16.9% and 3.4% of Brandt.[51]

To check the applicability of Eqs. (53) and (54) the second virial coefficients[58] and viscosities[59] of Freons are calculated. The estimated parameters are given in the lower part of Table 14. Dipole moments and polariza-bilities are taken from Landolt-Börnstein Tables.[34] The values of dipole moments in debye unit are 0.45, 0.51 and 1.29 and polarizabilities in $\overset{o}{A}^3$ of 8.24, 6.34, and 4.50 for Freon-11, Freon-12, and Freon-21, respectively. The polarizability of Freon-21, was calculated by Brandt[51] from the bond polarizabilities.

The calculated second virial coefficients and viscosities with the estimated parameters are compared with experiments in Tables 15 and 16. The agreement is surprisingly good for both properties. However, the overall agreement in Freon-21 calculations is only fair. Since the polarizability comes in every step of the calculation, we would rather suspect the accuracy of the calculated polarizability of Freon-21.

As for Eq. (53) the coefficient of 0.727 is smaller than that of nonpolar molecules. According to Cook and Rowlinson's[58] treatments of elliptical and polar molecules, the effect of asymmetry and dipole moment makes the critical temperature higher than that corresponding to spherical, nonpolar molecules. For polar molecules they obtained the relationship:

$$T_c^d = T_c^o(1 + 4\ \delta_c) \tag{55}$$

where subscript c denotes critical values and superscripts d and o denote dipolar and hypothetical nonpolar molecules. They obtained values of δ_c from the consideration of the corresponding states principle on vapor pressure as follows: 0.012 for H_2S, 0.028 for HCl and 0.012 for HBr. When averaged we have δ_c = 0.0173 which in turn gives T_c^d = 1.07 T_c^o. From Eq. (53) and that for nonpolar gases, i.e., ϵ^*_c/k = 0.78 T_c as used by them, we obtain T_c^d = 1.07 T_c^o which in some sense confirms the validity of Eq. (53).

Turning to the empirical equation for $\epsilon^o r^{o^{\epsilon}}$, there can be some explanation[51] on the exponent. That is, the omission of higher dipole-dipole interaction terms should be counterbalanced by the use of higher exponent. The value of 0.5985 lies between theoretical value of 0.5 and Brandt's value of 0.62. However, Brandt used Slater-Kirkwood's formula instead of Mavroyannis-Stephen. In

the present potential model dipole-induced dipole interaction is accounted for and the exponent seems reasonable.

In conclusion it is felt that the method of estimating parameters from critical temperatures and polarizabilities seems satisfactory. Nevertheless, if there are empirical parameters available, they should be preferred to those estimated.

CHAPTER VII

CORRESPONDING STATES CORRELATION FOR
TRANSPORT PROPERTIES OF GASES

The principle of corresponding states has been
widely used for the correlation of both equilibrium and
nonequilibrium properties of fluids.[32] Pitzer[53] has
proved the principle on the statistical mechanical basis
by moulding the partition function into a reduced variable
form with several assumptions. The reducing parameters
can be the critical constants, the potential parameters
or something else. When the Lennard-Jones 12-6 potential
is chosen as the universal potential energy function,
the simple spherical nonpolar molecules follow exactly
the principle of corresponding states. For polyatomic
molecules Trappeniers[55] formulated a new principle of
corresponding states by improving the crude spherical
approximation for the potential field. Cook and Rowlinson[56]
treated the elliptical and polar molecules by the use of
angle-dependent potential model. Guggenheim and Wormald[60]
accounted for the systematic deviations of hydrocarbons
from the principle of corresponding states by introducing
an additional parameter. Thodos and co-workers[61,62]
derived equations for transport properties of gases by

dimensional analysis with the critical constants. Their
results were successful for simple molecules.

According to the principle of corresponding states
the reduced properties of materials should be a universal
function of reduced temperature and pressure for the
classical mechanics. With the potential energy function
parameters as reducing variables we have the reduced
viscosity and diffusion coefficients as follows,[63]

$$\eta^* = \eta \; \sigma^3 / M^{\frac{1}{2}} \; \epsilon^{\frac{1}{2}} \tag{56}$$

$$D^* = DM^{\frac{1}{2}} / \sigma \; \epsilon^{\frac{1}{2}} \tag{57}$$

where the same symbolism as before is used. The main
drawback in the above scheme is that the potential
parameters should be known for the molecules under considera-
tion. Unfortunately, potential parameters are not always
known. Thus, instead of them the critical constants are
frequently used.

In this chapter the saturated liquid density parameters
at low pressure are used as the reducing variables. Reed[64]
has shown that the dependence of saturated liquid density
on temperature for $T < 0.8T_c$ can be expressed as:

$$\rho^2 = \underline{A} - \underline{B}T \tag{58}$$

where ρ is the molar density, $\underline{A}$ and $\underline{B}$ are positive constants.
Reed and McKinley[52] have shown that these parameters are
related to the parameters of the generalized n-m potential

by employing the smoothed potential cell model for liquid
phase and n-m potential for gas phase. Thus, the relation-
ships are:

$$\frac{\underline{A}}{\underline{B}} = (\epsilon/k) \ C_1 \tag{59}$$

$$\underline{A} = C_2/ r^{*e} \tag{60}$$

where C's are constants characteristic to the exponents
n and m. By combining Eqs. (56) and (57) with (59) and
(60) the reduced properties of gases are obtained.

$$\eta^{\neq} = \eta \ \underline{B}^{\frac{1}{2}}/(M^{\frac{1}{2}} \ \underline{A}^{5/e} \ k^{\frac{1}{2}}) \tag{61}$$

$$D^{\neq} = DM^{\frac{1}{2}} \ \underline{B}^{3/2}/(\underline{A}^{11/e} \ k^{3/2}) \tag{62}$$

The reduced viscosity and diffusion coefficients are now
functions of reduced temperature and pressure. The
reduced temperature, $T^{\neq}$ is here $T\underline{B}/\underline{A}$.

The experimental viscosities of simple molecules
are reduced by Eq. (61). These are at pressure one
atmosphere or less. The values of $\underline{A}$ and $\underline{B}$ used are given
in Table 17 where the sources of experimental density data
are also given. By the least-squares method the reduced
viscosities are obtained in terms of reduced temperatures
for eight molecules.

$$n^{\neq} = 91.6784 + 1145.764T^{\neq} - 91.2258T^{\neq\,2}$$
$$+ 4.1359T^{\neq\,3} - 0.00323T^{\neq\,5} \qquad (63)$$

This equation is obtained for the temperature range of $0.4 \leq T^{\neq} \leq 18.4$. Noting that reduced viscosities of Ar, Kr, O_2 and N_2 fall close to each other a different equation is obtained for these molecules,

$$n^{\neq} = -9.0278 + 1348.23877T^{\neq} - 183.03746T^{\neq\,2}$$
$$+ 14.47739T^{\neq3} - 0.04108T^{\neq\,5} \qquad (64)$$

for the temperature range of $0.4 \leq T^{\neq} \leq 9.1$.

The experimental diffusion coefficients at one atmosphere are also reduced by Eq. (62). When the reduced diffusion coefficients are plotted against reduced temperatures it appears that they could be best represented by two straight lines. By the least-squares fit the following two equations are obtained.

$$D^{\neq} \times 10^{20} = 9.12T^{\neq\,1.9039}, \quad 0.3 \leq T^{\neq} \leq 3.5 \qquad (65)$$

$$D^{\neq} \times 10^{20} = 11.36T^{\neq\,1.6427}, \quad 3.5 \leq T^{\neq} \leq 49.3 \qquad (66)$$

The results of viscosity calculations are given in Table 18 where the number of data points, temperature range, percent deviation and the sources of experimental data are also given. For the 168 data points of eight molecules used in the calculation the average deviation is 5.65%.

In general the deviation becomes large as the molecules become more complex. The reduced viscosities of Ne and Ar at low temperatures are very close but at high temperatures the Ar viscosities fall below those of Ne. This trend has been noticed previously by others.[36,37] In this calculation the reduced viscosities of N_2 and O_2 are very close to those of Ar. Therefore, the experimental data of Ne at high temperatures are rather suspected in spite of the conclusion of Mason and Rice[36] that the argon viscosities are low at high temperatures in view of the results of energy beam scattering experiments. The discrepancies in the reduced viscosities of Kr and Xe were also noted by them.

When only Ar, Kr, O_2 and N_2 are considered the average deviation is 1.18% for 105 data points. Here Kr shows the largest deviation among them all.

The summary of diffusion coefficient calculations is given in Table 19. For 51 data points of seven molecules the overall deviation is 4.2%. The agreement is good for simple molecules such as Ar, Kr, O_2 and N_2. However, it is poor for CH_4 and CF_4. It should be noted that the scatter of the experimental data is quite large for most of the molecules considered here. Thus, the deviation seems rather satisfactory.

In this correlation it has been implicit that all the molecules obey a particular n-m potential energy function. Yet it is a well-known fact that this is not true. That is, the 12-6 potential is good for small spherical molecules while 28-7 potential is better for polyatomic molecules than the 12-6 model. Thus, from the theoretical consideration it is hard to expect that the molecules considered here should follow the same corresponding states. As illustrated at the beginning of this chapter, complex molecules should be treated separately and we should be content with the results of these calculations which compare favorably with others.[61,61]

Table 1

Parameters for the Hard-Core Morse Potential

	$\epsilon/K°$,K	σ,Å	a,Å	c	No. of Data Pts.	Temp. Range °K	Rms.Dev. cc./mole	Ref.
Ar	133.7	3.3816	0.6738	2.8677	42	84-873	0.95	16
Kr	186.2	3.6417	0.6731	2.9677	31	109-873	1.35	68*,69,70
CO_2	524.4	3.5440	1.0366	3.6141	9	373-873	0.78	71
SF_6	413.8	4.7863	0.6374	5.0209	15	293-448	3.34	72
CF_4	200.4	4.6281	1.1363	2.6896	7	273-673	0.74	73
CH_4	161.0	3.7865	0.8651	2.5455	16	273-623	0.16	74
C_2H_6	430.4	3.8859	0.8705	2.5473	8	273-511	1.06	75**
C_3H_8	597.3	4.0859	0.8989	3.8566	27	295-511	3.92	75,58***,7?
C_4H_{10}	672.5	4.7789	1.0124	4.2538	16	423-478	2.30	75,58,7?
neoC_5H_{12}	508.0	5.8319	0.6476	5.0691	16	303-548	1.53	16

* Datum at 107°K not used.

** Datum at 310.9°K on C_3H_8 and data at 344.3 and 510.9°K on C_4H_{10} not used.

*** Deschner and Brown's data not used.

Table 2

Potential Parameters for Nonpolar Molecules

Molecule	Potential	$\epsilon/k, °K$	$\sigma, \overset{\circ}{A}$	C	Ref.
Ar	L-J	117.7	3.504	-	16
	Morse	119.53	3.5149	4.533	79
Kr	L-J	164.0	3.827	-	16
	Morse	192.24	3.6257	4.848	79
CO_2	L-J	198.2	4.328	-	16
SF_6	L-J	188.7	5.910	-	32
CF_4	L-J	151.5	4.744	-	16
CH_4	L-J	148.9	3.783	-	16
	Morse	203.5	3.6463	5.374	79
C_2H_6	L-J	230.0	4.418	-	32
	Morse	469.01	3.7417	6.721	17
C_3H_8	L-J	254.0	5.061	-	32
	Morse	527.81	4.3212	6.496	17
C_4H_{10}	L-J	410.0	4.997	-	32
	Morse	650.0	5.0665	7.751	17
$NeoC_5H_{12}$	L-J	232.5	7.445	-	16

Table 3

Critical Volumes and Polarizabilities

	V_c,cc./mole	V_c Ref.	α ,$\overset{\circ}{A}{}^3$	α Ref.
Ar	74.52	80	1.626	34
Kr	92.29	80	2.456	34
CO_2	94.2	25	2.65	34
SF_6	199	25	6.55	34
CF_4	138	64	4.02	34
CH_4	99	25	2.60	34
C_2H_6	148.2	25	4.47	34
C_3H_8	200.6	25	6.29	34
C_4H_{10}	255.1	25	8.12	34
$NeoC_5H_{12}$	303.5	25	10.36	34

Table 4

Cross Second Virial Coefficients of Binary Gas Mixtures

System	T°K	Expt.,cc./mole	Expt. - Calc.			Ref.
			Hard-Core	Morse	12-6	
Ar+Kr	108.001	236.16	+4.57[f]	+4.20[f]	+5.08[f]	68
	110.567	224.95	+5.41	+5.15	+6.67	
	113.272	216.14	+4.04	+3.89	+5.98	
	115.315	207.99	+4.98	+4.89	+7.36	
	117.083	206.72	+0.31	+0.26	+3.02	
	117.357	204.26	+1.87	+1.83	+4.64	
	119.002	198.42	+2.45	+2.45	+5.50	
	120.780	193.74	+1.68	+1.72	+5.00	
	123.616	186.44	+0.76	+0.85	+4.46	
CH$_4$+Ar	108.61	252.9	−29.8	−20.3	−34.7	70
	142.6	138.6	− 3.8	+ 0.2	− 2.7	
	176.7	86.7	+ 2.9	+ 4.3	+ 5.2	
	239.8	48.1	− 1.4	− 1.0	+ 0.7	
	295.0	26.9	0.0	− 0.2	+ 1.4	

Table 4 (Continued)

System	T°K	Expt.,cc./mole	Expt. Calc. Hard-Core	Morse	12-6	Ref.
$CH_4+C_2H_6$	273.2	11.19	-9.1	-5.1	-4.1	75
	298.2	92.0	-7.2	-4.1	-2.4	
	323.2	75.6	-5.3	-2.6	-0.5	
$CH_4+C_3H_8$	310.9	122.9	-12.9	-3.3	-8.0	75
	344.3	98.6	-11.3	-3.6	-7.4	
	377.6	80.2	-10.5	-4.2	-6.4	
	444.3	55.1	-10.6	-6.2	-8.3	
	510.9	34.8	- 7.5	-4.3	-7.1	
$CH_4+C_4H_{10}$	344.3	128.1	-9.9	-3.8	+6.7[f]	75
	377.6	97.9	-3.6	+0.5	+13.2	
	410.9	79.1	-3.8	-1.1	+13.1	
	444.3	60.4	-0.5	+1.1	+17.1	
	477.6	49.7	-2.5	-1.7	+14.9	
	510.9	42.9	-6.3	-6.1	+10.6	

Table 4 (Continued)

| System | T°K | Expt.,cc./mole | Expt. Calc. | | | Ref. |
			Hard-Core	Morse	12-6	
CH_4+SF_6	313.2	85	-9^f		$+4^f$	81
	333.2	68	-4		$+7$	
	353.2	57	-3		$+6$	
	373.2	45	0		$+7$	
	393.2	33	$+4$		$+10$	
$CH_4+NeoC_5H_{12}$	303.2	165	-20^f		$+15^f$	81
	323.2	138	-14		$+16$	
	333.2	132	-17		$+11$	
	343.2	118	-11		$+14$	
	353.2	113	-14		$+9$	
	363.2	106	-14		$+7$	
	383.2	93	-15		$+3$	
	403.2	78	-11		$+3$	

Table 4 (Continued)

| System | T°K | Expt.,cc./mole | Expt. Calc. | | | Ref. |
			Hard-Core	Morse	12-6	
CH_4+CO_2	310.9	63.8	-14.8		+3.9	82
	344.2	48.2	-12.2		+4.4	
	377.5	36.6	-10.5		+4.1	
	410.9	27.4	- 9.2		+3.6	
	444.2	19.8	- 7.0		+3.1	
	477.5	13.6	- 7.1		+2.6	
	510.8	8.4	- 6.3		+2.0	
CH_4+CF_4	273.16	62.07	+ 6.48[f]		+8.47[f]	83
	298.16	48.48	+ 5.85		+7.88	
	303.16	46.09	+ 5.75		+7.76	
	323.16	37.36	+ 5.42		+7.34	
	348.16	28.31	+ 4.90		+6.64	
	373.16	20.43	+ 4.75		+6.26	
	398.16	13.98	+ 4.37		+5.63	
	423.16	8.33	+ 4.14		+5.16	

Table 4 (Continued)

System	T°K	Expt.,cc./mole	Expt. Calc.			Ref.
			Hard-Core	Morse	12-6	
	448.16	3.21	+4.17		+4.93	
	473.16	-1.02	+3.95		+4.45	
	498.16	-4.94	+3.95		+5.46	
	523.16	-8.28	+3.81		+9.21	
	548.16	-11.39	+3.82		+12.70	
	573.16	-14.10	+3.76		+3.29	
	598.16	-16.55	+3.71		+5.77	
	623.16	-18.88	+3.79		+8.13	
$C_2H_6 + CO_2$	310.9	103.0	+17.8[f]		+22.5[f]	82
	344.2	87.5	+ 7.0		+13.4	
	377.5	73.3	+ 1.5		+ 9.2	
	410.9	60.4	- 0.9		+ 6.6	
	444.2	48.2	- 0.8		+ 6.0	
	477.5	37.0	+ 0.8		+ 6.4	
	510.8	26.0	+ 3.4		+ 8.3	

Table 4 (Continued)

System	T°K	Expt.,cc./mole	Expt. Calc.			Ref.
			Hard-Core	Morse	12-6	
$C_3H_8+CO_2$	310.9	154.5	+18.3[f]		+11.3[f]	75
	344.3	128.7	+ 6.9		+ 5.1	
	377.6	94.3	+14.0		+14.7	
	444.3	61.2	+ 9.9		+12.2	
	477.6	51.0	+ 6.9		+ 8.5	
	510.9	42.0	+ 5.2		+ 5.7	
$C_4H_{10}+CO_2$	377.6	130.6	− 3.4[f]		+31.0[f]	75
	410.9	100.3	+ 1.9		+35.8	
	444.3	80.6	+ 2.0		+33.6	
	477.6	65.0	+ 1.9		+32.5	

Table 5

Parameters for the 12-6-6 Potential Determined from Viscosities

Gas	$\epsilon°/k$, °K	$r°$, Å	μ, debye.	α, Å³	Reference
NH_3	168.4	3.842	1.47	2.26	84,85,86,87
H_2O	200.1	3.439	1.85	1.49	35,84,87,99
SO_2	257.1	4.702	1.63	3.72	87,88,89,90,91,92
HCl	256.9	3.910	1.08	2.63	93,94
HI	318.1	4.621	0.42	5.44	91,93,95
CH_3Cl	213.2	5.015	1.87	4.56	84,87,89,96
CH_2Cl_2	352.6	5.464	1.57	6.48	84
$CHCl_3$	350.1	5.960	1.013	8.23	84,87,97,98
CH_3OH	247.2	4.528	1.70	3.23	96,98
C_2H_5OH	283.3	5.276	1.69	5.62	97,98
$(CH_3)_2CO$	154.9	6.376	2.88	6.33	96,98

Table 6

Second Virial Coefficient for Polar Gases

NH_3

$t°C.$	-B cc/mole	
	calc.	expt.
-30	329	560
0	232	367
30	174	261
60	136	197
100	101	143
150	73	103
200	54	77
250	40	59

H_2O

$t°C.$	-B cc./mole	
	calc.	expt.
150	534	284
200	315	197
300	154	112
400	92	72

Table 6 (Continued)

SO_2		-B cc./mole	
	t°C.	calc.	expt.
	10	328	500
	20	304	452
	30	283	404
	40	265	367.5
	50	248	332.8
	75	212	279
	100	184	232.5
	125	160	201.0
	150	141	171.1
	175	124	144.1
	200	110	125.8

CH_3Cl		-B cc./mole	
	t°C.	calc.	expt.
	-34	508	764
	-23	457	668
	-18	436	637
	+10	344	500
	38	279	401
	65	232	320
	93	194	265
	121	164	214
	149	140	184
	177	120	155

Table 7

Empirical and Theoretical Dispersion
Attraction Constants

Polar Molecules	$\epsilon^o r^{o6}$, erg. $\times$ Å^6 $\times 10^{12}$		$\dfrac{\text{Empirical}}{\text{Theoretical}}$
	Empirical	Equation 12	
NH_3	74.7	67.6	1.105
H_2O	45.7	36.2	1.26
SO_2	383	255	1.50
HCl	127	114	1.11
HI	427	587	0.727
CH_3Cl	468	312	1.50
CH_2Cl_2	1295	672	1.93
$CHCl_3$	2160	1131	1.91
CH_3OH	294	155	1.89
C_2H_5OH	843	427	1.97
$(CH_3)_2CO$	1436	566	2.54
Nonpolar Molecules			
Ne	4.50	4.38	1.03
Ar	54.6	55.36	0.99
Kr	116	145.3	0.80
Xe	281	369.9	0.76
N_2	62.8	53.75	1.17
O_2	51.1	49.09	1.04
CH_4	128.9	88.2	1.46
CCl_4	3731	2004	1.86

Table 8

Potential Parameters and Molecular Constants
for Nonpolar Molecules

Molecules	$\varepsilon/k., °K$	$r, \overset{\circ}{A}$	$\alpha, \overset{\circ}{A}^3$	Ref.
H_2	37.0	3.287	0.79	30
N_2	91.5	4.132	1.76	30
O_2	113.0·	3.853	1.60	30
CH_4	144.0	4.261	2.60	30
C_2H_4	205.0	4.750	4.26	30
CO_2	190.0	4.485	2.65	30
CCl_4	327.0	6.601	10.50	30
He	10.22	2.869	0.204	30
Ne	35.7	3.131	0.393	30
Ar	124.0	3.837	1.626	30

Table 9

Viscosities of Binary Mixtures

System	T°K	X polar*	ɳx10⁷	calc.-expt. % dev.	Ref.
NH₃+H₂	293.16	0.9005	1003	-0.1	86
		0.7087	1045	-0.2	
		0.5177	1080	0.0	
		0.2975	1088	+0,1	
		0.2239	1073	+0.1	
		0.1082	1013	+0.2	
	373.16	0.9005	1335	+2.8	86
		0.7087	1361	+2.1	
		0.5177	1372	+1.3	
		0.2975	1338	+0.7	
		0.2239	1303	+0.3	
		0.1082	1207	+0.2	
	473.16	0.9005	1726	+4.0	86
		0.7087	1730	+3.0	
		0.5177	1711	+2.1	
		0.2975	1627	+1.1	
		0.2239	1572	+0.8	
		0.1082	1438	+0.4	
	523.16	0.9005	1906	+4.4	86
		0.7087	1900	+3.43	
		0.5177	1865	+2.3	
		0.2975	1756	+1.1	
		0.2239	1690	+0.7	

X = mole fraction

Table 9 (Continued)

System	T°K	X polar	$n \times 10^7$	calc.-expt. %dev.	Ref.
NH$_3$+N$_2$	293.16	0.8883	1094	+0.2	86
		0.7147	1261	+0.6	
		0.5638	1392	+0.7	
		0.2920	1594	+0.6	
		0.1111	1698	+0.5	
	373.16	0.8883	1434	+2.6	86
		0.7147	1601	+2.0	
		0.5638	1731	+1.2	
		0.2920	1930	+0.5	
		0.1111	2033	+0.1	
	473.16	0.8883	1830	+3.5	
		0.7147	1990	+2.3	
		0.5638	2115	+1.4	
		0.2920	2306	+0.4	
		0.1111	2409	0.0	
	523.16	0.8883	2013	+3.8	86
		0.7147	2169	+2.7	
		0.5638	2291	+1.8	
		0.2920	2480	+0.8	
		0.1111	2583	+0.4	
NH$_3$+O$_2$	293.16	0.8755	1139	-0.3	86
		0.7079	1343	-0.5	
		0.4786	1602	-0.1	

Table 9 (Continued)

System	T°K	X polar	$\eta \times 10^7$	calc.-expt. % dev.	Ref.
		0.2986	1783	0.0	
		0.1351	1927	+0.2	
	373.16	0.8755	1489	+2.1	86
		0.7079	1707	+1.0	
		0.4786	1982	+0.5	
		0.2986	2174	+0.2	
		0.1351	2329	+0.1	
	473.16	0.8755	1896	+3.0	86
		0.7079	2123	+1.8	
		0.4786	2409	+0.8	
		0.2986	2611	+0.3	
		0.1351	2778	+0.2	
NH_3+CH_4	287.66	0.9	990	-1.8	100
		0.8	1019	-1.9	
		0.7	1043	-1.7	
		0.6	1063	-1.3	
		0.5	1078	-1.2	
		0.4	1087	-1.1	
		0.3	1092	-1.2	
		0.2	1090	-1.3	
		0.1	1083	-1.5	

Table 9 (Continued)

System	T°K	X polar	$n \times 10^7$	calc.-expt. % dev.	Ref.
$NH_3+C_2H_4$	293.16	0.8867	1013	+1.2	86
		0.8071	1030	+1.7	
		0.6961	1047	+2.4	
		0.5172	105⁹	+2.7	
		0.2993	1049	+2.1	
		0.1096	1027	+1.2	
	373.16	0.8867	1335	+3.2	86
		0.8071	1342	+3.2	
		0.6961	1345	+3.1	
		0.5172	1338	+2.7	
		0.2993	1312	+1.6	
		0.1096	1277	+0.6	86
	473.16	0.8867	1712	+3.9	
		0.8071	1704	+3.4	
		0.6961	1689	+3.1	
		0.5172	1657	+2.2	
		0.2993	1609	+0.9	
		0.1096	1561	+0.0	
	523.16	0.8867	1886	+4.3	86
		0.8071	1871	+3.7	
		0.6961	1848	+3.2	
		0.5172	1805	+2.3	
		0.2993	1747	+1.0	
		0.1096	1693	+0.2	

Table 9 (Continued)

System	T°K	X polar	$n \times 10^7$	% calc.-expt. dev.	Ref.
HCl+H_2	294.6	0.8220	1451	-0.7	94
		0.7179	1459	-0.6	
		0.5042	1460	-0.7	
		0.2031	1331	-0.8	
	327.16	0.8220	1617	-0.6	94
		0.7179	1623	-0.6	
		0.5042	1614	-0.7	
		0.2031	1451	-1.4	
	372.16	0.8220	1839	-0.5	94
		0.7179	1840	-0.8	
		0.5042	1816	-0.8	
		0.2031	1607	-1.4	94
	427.16	0.8417	2099	0.0	
		0.6989	2094	-0.5	
		0.5092	2057	+0.2	
		0.2409	1855	-0.6	
	473.16	0.8417	2307	-0.2	94
		0.6989	2296	-0.3	
		0.5092	2245	-0.7	
		0.2409	2008	-0.8	
	523.16	0.7947	2520	-0.3	94
		0.6312	2489	-0.7	
		0.5178	2446	-0.3	
		0.2991	2256	-1.1	

Table 9 (Continued)

System	$T°K$	X polar	$n \times 10^7$	% calc.-expt. dev.	Ref.
HCl+CO_2	291.16	0.9	1426	-2.3	100
		0.8	1437	-2.4	
		0.7	1445	-2.6	
		0.6	1451	-2.7	
		0.5	1456	-2.9	
		0.4	1459	-2.9	
		0.3	1460	-2.9	
		0.2	1459	-2.7	
		0.1	1457	-2.5	
SO_2+H_2	290.16	0.8215	1273	-1.5	90
		0.5075	1333	-1.3	
		0.2963	1346	-1.7	
		0.2286	1330	-1.0	
		0.1676	1294	-0.8	
	318.16	0.8028	1409	-1.1	90
		0.5075	1462	-0.9	
		0.2963	1464	-1.3	
		0.2286	1441	-0.8	
		0.1676	1397	-0.9	
	343.16	0.8028	1527	-0.5	90
		0.6999	1545	-0.8	
		0.6175	1559	-1.0	
		0.4823	1577	-0.6	

Table 9 (Continued)

System	T°K	X polar	nx10^7	calc.-expt. % dev.	Ref.
		0.2963	1568	-1.8	
		0.2306	1540	-0.7	
		0.1676	1487	-0.9	
		0.1657	1485	-1.3	
	365.16	0.8028	1628	-0.3	90
		0.6999	1646	-0.1	
		0.6175	1659	-1.0	
		0.4823	1674	-0.5	
		0.2306	1624	-1.0	
		0.1676	1564	-0.6	
		0.1657	1562	-1.0	
	397.16	0.6760	1793	-0.2	90
		0.4698	1813	-0.1	
		0.3265	1796	-0.3	
		0.1636	1673	-0.7	
	432.16	0.6760	1946	+0.2	90
		0.4698	1960	0.0	
		0.3265	1934	-0.4	
		0.1676	1797	-0.3	
		0.1512	1769	+1.2	
	472.16	0.6760	2115	-0.1	90
		0.4905	2123	+0.1	
		0.3265	2085	-0.6	
		0.1512	1893	-3.1	

Table 9 (Continued)

System	T°K	X Polar	$n \times 10^7$	calc.-expt. % dev.	Ref.
SO_2+CO_2	288.96	0.9	1262	-2.0	100
		0.8	1289	-2.1	
		0.7	1316	-1.6	
		0.6	1340	-1.7	
		0.5	1364	-1.4	
		0.4	1385	-1.6	
		0.3	1404	-1.7	
		0.2	1421	-1.8	
		0.1	1434	-2.0	
$CH_2Cl_2+CCl_4$	293.15	0.8425	987	-3.3	101
		0.6985	989	-2.7	
		0.5014	988	-2.5	
		0.3114	985	-1.5	
		0.1484	981	-1.0	
	353.16	0.6739	1196	-1.3	101
		0.3649	1190	-0.1	
	413.43	0.8485	1403	-1.5	101
		0.7118	1401	-0.1	
		0.5264	1396	-1.1	
		0.2904	1387	+0.4	
		0.1261	1380	+0.9	

Table 10

Diffusion Coefficients of Binary Mixtures

System	$T^{\circ}K$	D_{12}	calc.-expt. % dev.	Ref.
H_2O+H_2	293.11	0.828	-2.6	102
	322.66	0.981	-3.0	
	365.56	1.221	-1.0	
	372.50	1.261	-1.6	
	307.26	0.900	-11.8	103
	328.56	1.013	-9.6	
	352.66	1.147	-4.4	
	307.16	0.900	-1.6	104
	328.66	1.014	+5.5	
H_2O+N_2	307.56	0.254	-0.8	103
	328.56	0.287	-5.3	
	352.16	0.326	-9.2	
	328.96	0.288	-8.0	104
	349.16	0.321	-9.3	
H_2O+O_2	308.06	0.258	-8.5	103
	328.96	0.292	-8.2	
	352.36	0.331	-6.0	
	400.00	0.417	-13.1	40
	500.00	0.621	-8.7	
	700.00	1.118	-6.8	
	900.00	1.718	-6.6	
	1050.00	2.230	-6.7	

Table 10 (Continued)

System	T°K	D_{12}	calc.-expt. % dev.	Ref.
H_2O+CO_2	296.11	0.175	+6.7	102
	365.56	0.261	+5.2	
	372.54	0.270	+4.2	
	307.46	0.188	-6.9	103
	328.56	0.213	+0.9	
	352.36	0.243	-0.8	
	328.66	0.213	+7.6	104
H_2O+CH_4	307.66	0.257	-12.1	103
	328.76	0.291	-12.1	
	352.26	0.331	- 7.0	
$H_2O+C_2H_4$	307.76	0.186	- 8.8	103
	328.46	0.211	- 9.4	
	352.56	0.241	- 2.4	
H_2O+He	307.16	0.880	- 2.4	103
	328.16	0.984	- 2.7	
	352.46	1.109	- 1.1	
	298.16	0.837	- 7.8	105
NH_3+H_2	298.16	0.785	+ 0.3	30
	328.16	0.927	- 1.7	
	358.16	1.078	- 1.4	
	263.0	0.630	+10.5	106
	328.0	0.926	+ 2.9	

Table 10 (Continued)

System	T°K	D_{12}	calc.-expt. % dev.	Ref.
	395.0	1.276	− 5.5	
	473.0	1.734	− 6.3	
NH_3+N_2	298.16	0.229	− 4.3	30
	328.16	0.272	− 4.6	
	358.16	0.318	− 3.0	
SO_2+H_2	285.56	0.528	+ 0.6	107
	263.00	0.456	+ 6.0	106
	323.00	0.657	+ 7.7	
	473.00	1.272	+ 3.4	
SO_2+N_2	263.00	0.101	− 2.9	106
SO_2+CO_2	263.00	0.069	+ 7.8	106
	343.00	0.116	+ 7.4	
	473.00	0.212	+ 8.7	
$C_2H_5OH+H_2$	340.16	0.623	+ 6.3	102
$C_2H_5OH+CO_2$	340.16	0.107	+ 1.0	102
C_2H_5OH+He	298.16	0.459	− 7.1	105
$(CH_3)_2CO+H_2$	296.16	0.411	− 3.1	102

Table 11

Potential Parameters for the 12-6-6 Potential
Determined rom the Second Virial Coefficients

	$\epsilon^{\circ}/k, {}^{\circ}K$	$r^{\circ}, \text{Å}$	$\dfrac{\epsilon^{\circ}r^{\circ 6}\ \text{Emp.}}{\epsilon^{\circ}r^{\circ 6}\ \text{Theor.}}$
NH_3	203.4	3.601	0.906
H_2O	234.8	3.670	2.188
SO_2	267.1	3.843	0.466
CH_3Cl	248.0	4.510	0.923
C_2H_5Cl	344.7	4.785	0.962
CH_3CN	157.7	5.447	2.039
CH_3CHO	167.9	5.040	1.322
$(CH_3)_2CO$	284.1	5.216	1.395

Table 12

Joule-Thomson Coefficients at Zero Pressure

System	T°C.	Expt.,°K/atm.	Expt.-Calc.	Expt.-Calc. % dev.
NH₃	-18	4.954	-1.590	-32.1
	-13	4.568	-1.354	-29.6
	- 5	4.045	-1.054	-26.0
	10	3.321	-0.643	-19.4
	30	2.591	-0.376	-14.5
	50	2.091	-0.221	-10.6
	70	1.725	-0.132	- 7.6
	110	1.224	-0.055	- 4.5
	150	0.938	-0.033	- 3.5
SO₂	50.7	3.020	-0.158	- 5.2
	101.6	2.166	+0.270	+12.5
	150.5	1.645	+0.350	+21.3
	200.2	1.315	+0.372	+28.3
H₂O	100	6.37	-0.52	- 8.2
	150	3.85	+0.15	+ 3.9
	200	2.48	+0.14	+ 5.6
	250	1.69	+0.06	+ 3.5
	300	1.20	0	0.0
	350	0.91	-0.02	- 2.2
	400	0.73	-0.01	- 1.4
	450	0.595	-0.013	- 2.2
	500	0.490	-0.016	- 3.3
	550	0.415	-0.012	- 2.9

Table 13

Empirical and Estimated Values of ε^{*}_{c}/kTc

	T_{c}, °K	Emp. ε^{*}_{c}/k, °K	ε^{*}_{c}/kTc	Calc.-Emp. %dev.
NH_3	405.6	347.8	0.857	-15
H_2O	647.0	855.9	1.323	-45
SO_2	430.4	327.7	0.761	-4.5
$(CH_3)_2CO$	508.7	247.4	0.486	+49
HCl	324.6	313.2	0.965	-25
HI	424.6	319.8	0.754	-3.5
CH_3Cl	416.3	299.6	0.720	-0.9
CH_2Cl_2	510.0	377.4	0.740	-1.7
$CHCl_3$	536.6	379.5	0.707	+2.8
CH_3OH	513.2	335.7	0.654	+11
C_2H_5OH	516.3	320.9	0.621	+17
Average			0.727	15.9

Table 14

Empirical and Estimated Potential Parameters for Polar Gases

	ε °/k Emp.	ε °/k Calc.	Calc.-Emp. % dev.	r° Emp.	r° Calc.	Calc.-Emp. % dev.
NH_3	168.4	154.0	-8.5	3.842	3.985	+3.7
H_2O	200.1	96.3	-51.9	3.439	3.805	+10.6
SO_2	257.1	250.2	- 2.7	4.702	4.792	+1.9
HCl	256.9	201.2	-21.7	3.910	4.230	+8.2
HI	318.1	308.1	- 3.1	4.621	5.464	+18.2
CH_3Cl	213.2	223.7	+ 4.9	5.015	5.083	+1.3
CH_2Cl_2	352.6	347.1	- 1.5	5.464	5.505	+0.7
$CHCl_3$	350.1	386.0	+10.2	5.960	5.999	+0.6
CH_3OH	247.2	254.2	+2.8	4.528	4.326	-4.5
C_2H_5OH	283.3	327.9	+15.7	5.276	5.077	-3.8
$(CH_3)_2CO$	154.9	203.2	+31.2	6.376	5.816	-8.8
Freon-11	—	342.1	—	—	6.203	—
Freon-12	—	278.9	—	—	5.857	—
Freon-21	—	310.1	—	—	5.117	—
Avg.			14.0			5.7

Table 15

Second Virial Coefficients of Freons*

T, °K	Freon-11		Freon-12		Freon-21	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
238.71	1150	1011	637	598	766	546
244.27	—	—	604	575	—	—
249.82	1070	934	586	553	734	502
255.38	—	—	560	532	—	—
283.16	862	751	454	445	616	399
310.94	720	639	347	377	528	337
338.71	617	551	—	—	446	289
366.49	523	480	—	—	403	250
394.27	459	421	—	—	354	218
422.05	381	372	—	—	310	191
449.82	328	331	—	—	271	169

* B in cc./mole

Table 16

Viscosities of Freon.

T°K	Freon-11		Freon-12		Freon-21	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
233.16	880	808	1060	945	940	1048
244.26	920	847	1090	991	980	1100
255.36	960	.886	1130	1037	1010	1152
266.46	990	926	1160	1082	1050	1204
277.56	1030	965	1190	1128	1080	1256
288.67	1060	1004	1230	1173	1110	1309
299.86	1100	1044	1260	1218	1150	1361
310.96	1130	1084	1290	1263	1180	1414
322.06	1160	1123	1320	1307	1210	1466
333.16	1200	1162	1350	1351	1240	1517
344.26	1230	1201	1380	1395	1270	1568
355.36	1260	1240	1400	1438	1300	1620
366.46	1290	1278	1430	1481	1330	1670
377.56	1320	1316	1460	1524	1360	1721
388.76	1350	1355	1490	1566	1390	1772

* $\eta \times 10^7$

Table 17

Liquid Density Parameter

	$A \times 10^4$ $Mole^2 \times cc.^{-2}$	$B \times 10^7$ $Mole^2 \times cc.^{-2} \times {}^\circ K^{-1}$	Ref.
Ne	64.9618	1088.63	108
Ar	22.2310	113.60	108
Kr	14.8306	54.7944	108
Xe	10.0281	27.2227	108
O_2	22.903	112.84	65, 76
N_2	15.540	93.779	65, 76
CH_4	12.2598	47.2576	64
CF_4	6.4629	21.4311	64

Table 18

Reduced Viscosities of Simple Gases

	No. of Data Pts.	$T^{\#}$ Range	% dev. Eq.(63)	% dev. Eq.(64)	Ref.
Ne	35	1.2-18.4	2.55	—	92,109,110,111,112,113,114
Ar	28	0.4-7.7	2.50	0.88	114,115
Kr	5	1.0-1.4	0.98	2.10	113,115
Xe	8	0.7-1.5	8.17	—	113,116
O_2	33	0.4-4.9	3.46	1.59	32,86,87,109,117,118,120
N_2	39	0.5-9.1	2.68	0.93	32,86,87,111,117,119,120
CH_4	11	0.4-1.2	8.08	—	32
CF_4	9	1.0-1.5	8.42	—	64
	168	0.4-18.4	3.65	1.18	

Table 19

Reduced Diffusivities of Simple Gases

	No. of Data Pts.	$T^{\neq}$ Range	% Dev.	Ref.
Ne	5	1.3-5.9	5.25	121
Ar	7	0.4-1.8	3.72	121
Kr	1	1.1	2.59	32
O_2	24	0.4-49.3	3.43	121,122
N_2	5	0.5-2.1	3.60	121
CH_4	5	0.3-1.4	4.67	121
CF_4	4	1.0-1.1	9.56	123
	51	0.3-49.3	4.20	

Appendix

Reduced Second Virial Coefficient B*(T*,c,a*) for the Hard-Core Morse Potential

C = 3.00

T* / a*	0.10000	0.30000	0.50000	0.70000	0.90000	1.10000	1.30000
0.3	-65.392054	-83.577211	-103.898321	-126.301350	-150.56311	-177.197224	-205.502067
0.4	-31.883098	-40.238871	-49.472044	-59.455987	-70.221116	-61.693828	-93.825511
0.5	-20.067638	-25.039839	-30.428038	-36.104233	-42.250420	-48.608603	-55.180776
0.6	-14.305790	-17.658428	-21.221408	-24.946727	-28.786303	-32.692369	-36.616692
0.7	-10.955976	-13.380889	-15.899565	-18.464002	-21.026198	-23.530154	-25.951860
0.8	-8.786849	-10.615733	-12.466403	-14.288840	-16.035071	-17.657074	-19.108845
0.9	-7.210757	-8.691615	-10.081591	-11.392077	-12.576872	-13.586175	-14.372582
1.0	-6.158062	-7.280268	-8.334945	-9.274091	-10.049700	-10.613773	-10.918308
1.1	-5.307635	-6.203382	-7.003095	-7.661472	-8.127813	-8.355013	-8.299070
1.2	-4.637597	-5.356196	-5.955202	-6.395617	-6.620436	-6.584655	-6.240073
1.3	-4.096747	-4.673300	-5.116156	-5.371317	-5.408778	-5.162529	-4.590593
1.4	-3.651483	-4.111820	-4.424550	-4.541669	-4.415180	-3.957080	-3.739361
1.5	-3.278370	-3.642523	-3.847043	-3.844491	-3.580200	-3.025999	-2.114073
1.6	-2.962727	-3.244814	-3.358139	-3.254700	-2.824494	-2.205521	-1.163781
1.7	-2.691322	-2.903769	-2.939267	-2.749804	-2.287389	-1.504011	-0.351678
1.8	-2.455949	-2.603327	-2.576720	-2.313150	-1.710593	-0.858052	0.349472
1.9	-2.250012	-2.350106	-2.260150	-1.932139	-1.310071	-0.369943	0.960243
2.0	-2.068418	-2.122653	-1.941538	-1.597070	-0.922252	0.093926	1.496461
2.2	-1.763147	-1.740871	-1.514492	-1.036006	-0.274437	0.809290	2.392115
2.4	-1.516947	-1.433604	-1.139261	-0.585915	0.274437	1.469793	3.108155
2.6	-1.314555	-1.181534	-0.831981	-0.217894	0.708727	1.995888	3.691589
2.8	-1.145522	-0.971450	-0.514342	0.087802	1.068900	2.415201	4.174463
3.0	-1.002454	-0.794909	-0.360022	0.345106	1.371702	2.762203	4.579376
3.2	-0.879978	-0.642439	-0.177072	0.564125	1.629151	3.066010	4.922706
3.4	-0.774098	-0.511690	-0.018872	0.752366	1.850020	3.322096	5.216595
3.6	-0.691777	-0.397946	0.118483	0.915513	2.041147	3.543366	5.470235
3.8	-0.600674	-0.298253	0.238622	1.057954	2.207744	3.735992	5.690704
4.0	-0.528951	-0.210297	0.344394	1.183120	2.353887	3.904695	5.883549
4.2	-0.465142	-0.132237	0.430058	1.293742	2.482818	4.052289	6.053155
4.4	-0.408073	-0.062595	0.521429	1.392005	2.597134	4.164316	6.203057
4.6	-0.356789	-0.000173	0.595987	1.479693	2.698948	4.301756	6.336114
4.8	-0.310498	0.056022	0.662943	1.558265	2.789995	4.406128	6.454677
5.0	-0.268551	0.106804	0.723298	1.628930	2.871704	4.492321	6.560687
6.0	-0.107584	0.300094	0.951268	1.893942	3.176117	4.845799	6.950985
7.0	-0.000464	0.426656	1.098236	2.062278	3.366780	5.059745	7.189181
10.0	0.169485	0.620205	1.314715	2.301015	3.627112	5.341004	7.490697
20.0	0.300124	0.740647	1.415576	2.372915	3.660668	5.326635	7.419419
50.0	0.281355	0.651928	1.234770	2.077882	3.229269	4.736931	6.648870
100.0	0.218747	0.521029	1.014622	1.747528	2.767751	4.123292	5.862152
200.0	0.152634	0.385838	0.787216	1.404769	2.286500	3.480411	5.034503
300.0	0.118538	0.313638	0.662709	1.213757	2.014783	3.113708	4.558776
400.0	0.097378	0.267176	0.580749	1.086099	1.831225	2.864134	4.232874

Reduced Second Virial Coefficient B*(T*,c,a*) for the Hard-Core Morse Potential

C= 4.00

T*/a	0.10000	0.50000	0.50000	0.50000	0.70000	0.90000	1.10000	1.30000
0.3	-42.341393	-57.945052	-58.07066		-49.9238	-101.710353	-90.121775	-79.864131
0.4	-20.188535	-25.818354	-008.177		-58.747177	-45.878211	-53.461581	-61.413420
0.5	-12.446652	-15.683630	-19.156636		-22.811616	-26.605583	-30.491576	-34.413503
0.6	-8.696962	-10.791587	-12.965966		-15.172094	-17.361972	-19.687600	-21.500036
0.7	-6.528653	-7.970281	-9.404232		-10.782499	-12.057086	-13.179985	-14.103197
0.8	-5.132424	-6.153682	-7.114777		-7.964701	-8.655456	-9.139041	-9.367451
0.9	-4.157209	-4.893826	-5.529280		-6.015562	-6.304675	-6.348617	-6.099301
1.0	-3.444992	-3.972392	-4.374145		-4.593245	-4.590692	-4.315485	-3.712610
1.1	-2.902370	-3.271133	-3.490747		-3.513002	-3.289000	-2.773748	-1.915611
1.2	-2.475570	-2.72027	-2.800480		-2.666762	-2.271598	-1.565900	-0.504906
1.3	-2.122022	-2.2780	-2.245820		-1.987307	-1.445415	-0.599446	0.625906
1.4	-1.849807	-1.914620	-1.791127		-1.430725	-0.765614	0.192211	1.550752
1.5	-1.614125	-1.611812	-1.412161		-0.967174	-0.728847	0.850821	2.319934
1.6	-1.414557	-1.355505	-1.091080		-0.575679	0.212097	1.406452	2.968302
1.7	-1.243556	-1.136118	-0.817963		-0.241090	0.642503	1.880819	3.521862
1.8	-1.095534	-0.946404	-0.581291		0.047808	0.988896	2.289974	3.990006
1.9	-0.966259	-0.780884	-0.374970		0.299489	1.270491	2.646042	4.414144
2.0	-0.852472	-0.635341	-0.193698		0.520463	1.505141	2.958339	4.770002
2.2	-0.661688	-0.391672	0.109424		0.889604	1.869008	3.479219	5.384659
2.4	-0.508369	-0.196244	0.352133		1.184764	2.249650	3.947007	5.868206
2.6	-0.382779	-0.036437	0.550203		1.425297	2.626796	4.232701	6.261015
2.8	-0.278266	0.096183	0.714406		1.624408	2.874192	4.511750	6.585111
3.0	-0.190131	0.207822	0.852233		1.791403	3.093035	4.745232	6.855957
3.2	-0.114963	0.302828	0.969489		1.933025	3.234436	4.942726	7.084097
3.4	-0.050229	0.384460	1.069961		2.054275	3.385906	5.111358	7.280132
3.6	0.005993	0.455192	1.156559		2.158941	3.509497	5.256512	7.447907
3.8	0.055186	0.516927	1.232510		2.249938	3.617212	5.382335	7.593309
4.0	0.098510	0.571161	1.298840		2.329550	3.711293	5.492049	7.719633
4.2	0.136887	0.619077	1.357309		2.399586	3.793910	5.588284	7.830709
4.4	0.171060	0.661627	1.409105		2.461500	3.866611	5.673042	7.928195
4.6	0.201632	0.699583	1.455196		2.516470	3.931410	5.749017	8.014294
4.8	0.229096	0.733583	1.496373		2.565468	3.938868	5.814579	8.090603
5.0	0.253865	0.764150	1.533290		2.609287	4.040145	5.813062	8.158444
6.0	0.347531	0.878653	1.670400		2.770774	4.227777	6.089413	8.403653
7.0	0.408071	0.951211	1.755697		2.869529	4.340711	6.211247	8.547137
10.0	0.497805	1.053467	1.869973		2.995327	4.477729	6.364582	8.704488
20.0	0.542007	1.081378	1.874558		2.969546	4.414348	6.256963	8.545395
50.0	0.472853	0.947972	1.660294		2.657822	3.988557	5.760502	7.841662
100.0	0.386868	0.799995	1.434509		2.338700	3.560299	5.147301	7.147958
200.0	0.298090	0.646388	1.198096		2.003196	3.107801	4.560603	6.409514
300.0	0.249620	0.560388	1.064608		1.810283	2.845415	4.218005	5.976657
400.0	0.217696	0.502533	0.973067		1.677299	2.663233	3.938871	5.672215

Reduced Second Virial Coefficient B*(T*,c,a*) for the Hard-Core Morse Potential

C= 5.00

T*	0.10000	0.30000	0.50000	0.70000	0.90000	1.10000	1.30000
0.3	-30.751?2	-40.276052	-50.946096	-62.?610	-7?.578671	-89.421017	-104.?52714
0.4	-14.375?05	-19.503?4?	-23.018?5?	-27.870?77	-33.014923	-38.397460	-43.9?771?
0.5	-8.603886	-10.987651	-13.376059	-15.862192	-18.376599	-20.872427	-23.?001?2
0.6	-5.939330	-7.344188	-8.750560	-10.110?35	-11.375131	-12.497930	-13.?2936?
0.7	-4.357874	-5.260?44	-6.095445	-6.813405	-7.366741	-7.707606	-7.7077?6
0.8	-3.340018	-3.922995	-4.392701	-4.701492	-4.801351	-4.644193	-4.182195
0.9	-2.635037	-2.997124	-3.215862	-3.243272	-3.031372	-2.532055	-1.667503
1.0	-2.119469	-2.321263	-2.357740	-2.180092	-1.742739	-0.995226	0.109560
1.1	-1.727274	-1.807792	-1.706435	-1.37188	-0.766061	0.168554	1.477861
1.2	-1.419584	-1.405431	-1.196528	-0.744650	-0.002426	1.078755	2.546726
1.3	-1.172197	-1.082282	-0.787350	-0.239392	0.609593	1.802588	3.402638
1.4	-0.969285	-0.817501	-0.452352	0.174167	1.110062	2.403318	4.101928
1.5	-0.800078	-0.596022	-0.173495	0.511204	1.526180	2.898427	4.682963
1.6	-0.657001	-0.410584	0.061894	0.806633	1.877037	3.315708	5.?7245C
1.7	-0.534573	-0.251291	0.262966	1.056200	2.17?411	3.671606	5.?9783
1.8	-0.428740	-0.113718	0.436492	1.269894	2.434487	3.978279	5.949264
2.0	-0.336434	0.006159	0.587567	1.455851	2.658953	4.244898	6.261682
2.2	-0.255294	0.111437	0.720181	1.610940	2.855714	4.478510	6.535376
2.?	-0.119915	0.297368	0.941515	1.890932	3.183617	4.867575	6.99081C
2.?	-0.010688	0.420109	1.118308	2.107913	3.444925	5.177346	7.353182
2.6	0.078215	0.542850	1.262226	2.28431?	3.657134	5.428678	7.446955
2.?	0.151993	0.637900	1.381228	2.429983	3.832164	5.635773	7.888317
3.0	0.214034	0.717653	1.480921	2.551838	3.978407	5.808631	8.09C513
3.?	0.266790	0.785327	1.565363	2.654900	4.101940	5.954455	8.26054C
3.4	0.312086	0.843302	1.637566	2.742886	4.207263	6.078056	8.405191
3.6	0.351303	0.893377	1.699813	2.816613	4.297780	6.185317	8.529225
3.8	0.385564	0.936942	1.753854	2.884244	4.376113	6.277464	8.636299
4.0	0.415523	0.975002	1.801064	2.941472	4.444309	6.357576	8.729217
4.2	0.442021	1.008650	1.842531	2.991641	4.503991	6.427584	8.810422
4.4	0.465530	1.038363	1.879128	3.035827	4.556462	6.489036	8.881551
4.6	0.486480	1.067758	1.911566	3.074905	4.602779	6.543188	8.944135
4.8	0.505227	1.088305	1.940425	3.109592	4.643305	6.591C7C	8.99938E
5.0	0.522064	1.109382	1.966186	3.140477	4.680257	6.633529	9.049297
6.0	0.584924	1.187276	2.060531	3.252689	4.811753	6.785725	9.22261C
7.0	0.624476	1.235212	2.117426	3.319119	4.888295	6.972955	9.321103
10.0	0.679169	1.297439	2.186784	3.395210	4.970716	6.961306	9.41499?
20.0	0.689403	1.290491	2.157026	3.337012	4.878449	6.929341	9.23769C
50.0	0.606571	1.150597	1.946787	3.043114	4.487568	6.320364	8.61222?
100.0	0.516830	1.006092	1.734944	2.751388	4.103626	5.849060	8.006294
200.0	0.423402	0.854474	1.511252	2.441737	3.693932	5.315840	7.355461
300.0	0.370798	0.766638	1.381642	2.260811	3.453147	5.C66655	6.965334
400.0	0.335173	0.707972	1.291731	2.134450	3.284133	4.788762	6.656192

Reduced Second Virial Coefficient B*(T*,c,a*) for the Hard-Core Morse Potential

c = 6.00

Tr / Δ*	0.1500	0.30000	0.50000	0.70000	0.90000	1.10000	1.3000
0.28	-29.5?751	-39.?00779	-49.719930	.608970	-46.?511	-86.557467	-103.562772
0.30	-23.5?.?3	-3?.401?9	-39.942541	297767	-59.447346	-70.370069	-66.023536
0.32	-19.765906	-29.955953	-32.834878	.368549	-58.514049	-57.222811	-66.446237
0.34	-16.707013	-21.832330	-27.511041	.690494	-40.336121	-47.546902	-56.750071
0.36	-14.335036	-18.627586	-23.715866	-28.561879	-34.047615	-39.025361	-45.842260
0.38	-12.464509	-16.155671	-20.190166	-24.190166	-29.027613	-33.874729	-39.802090
0.40	-10.960000	-14.144340	-17.598182	-21.273.17	-25.122647	-29.097356	-34.149705
0.42	-9.728796	-12.499423	-15.479336	-18.626046	-21.675276	-25.195337	-28.532709
0.44	-8.706206	-11.135682	-13.721734	-16.415929	-19.102384	-21.960276	-24.765724
0.46	-7.845761	-9.985667	-12.242379	-14.576045	-16.919901	-19.242049	-21.491615
0.48	-7.113408	-9.000804	-10.986517	-12.998517	-14.997016	-16.933766	-18.760929
0.50	-6.483720	-8.169300	-9.906856	-11.646417	-13.355091	-14.951514	-16.417106
0.55	-5.242550	-6.915646	-7.761860	-7.991591	-10.655.0	-11.654063	-11.809878
0.60	-4.331928	-5.304100	-6.222449	-7.044998	-7.123653	-0.204499	-0.424550
0.65	-3.695057	-3.600436	-4.167701	-6.415950	-4.509859	-4.350774	-3.694643
0.70	-2.300830	-2.606734	-2.766529	-2.732210	-2.455786	-1.889248	-0.594580
0.80	-1.791299	-1.878656	-1.844649	-1.657156	-1.040223	-0.153042	1.015590
0.90	-1.350203	-1.347971	-1.159973	-0.7??709	-0.010679	1.038622	2.469691
1.0	-1.145257	-0.945257	-0.641451	-0.060649	0.765908	1.971438	3.549534
1.1	-0.8067.0	-0.630046	-0.239021	0.414275	1.377910	2.699038	4.560037
1.2	-0.615054	-0.377159	0.005585	0.815173	1.865614	3.282906	5.115051
1.3	-0.457978	-0.170163	0.347456	1.142670	2.264106	3.759140	5.675903
1.4	-0.327134	0.002110	0.569909	1.41?266	2.595180	4.154653	6.141685
1.5	-0.216612	0.147498	0.751990	0.77?.709	2.874119	4.487761	6.523780
1.6	-0.122140	0.271667	0.909950	1.840711	3.111940	4.771668	6.867885
1.7	-0.0?0055	0.378805	1.046153	2.009490	3.316618	5.016137	7.155450
1.8	0.030530	0.412675	1.166649	2.156244	3.494370	5.228527	7.405215
1.9	0.092953	0.553969	1.266539	2.284646	3.650829	5.414492	7.623034
2.0	0.197255	0.690472	1.441740	2.499900	3.910439	5.723872	7.987362
2.2	0.220681	0.755507	1.579834	.665603	4.116993	5.969828	8.276168
2.4	0.346090	0.806852	1.?2040	.8001	4.284450	6.169070	8.509952
2.6	0.405006	0.981564	1.784639	2.922231	4.422342	6.332973	8.702126
2.8	0.442256	1.022969	2.109113	3.320356	4.547337	6.469941	8.862119
3.0	0.492341	1.074956	2.140640	3.017508	4.634266	6.584561	8.996754
3.2	0.526674	1.119307	2.160758	3.097727	4.716772	6.682321	9.111081
3.4	0.556323	1.157669	1.983306	3.166434	4.787509	6.766061	9.208916
3.5	0.562111	1.190867	2.031315	3.225201	4.848581	6.838272	9.293194
3.6	0.604683	1.219889	2.072890	3.276121	4.901618	6.909902	9.366208
4.0	0.624550	1.245348	2.109113	3.320356	4.947912	6.955493	9.429773
4.2	0.642121	1.267802	2.140640	3.359028	4.980496	7.003281	9.485345
4.4	0.657730	1.287690	2.168758	3.392989	5.024212	7.045268	9.534103
4.6	0.671650	1.305372	2.194424	3.422920	5.055745	7.022276	9.577013
4.8	0.684107	1.321142	2.215294	3.449418	5.003665	7.114961	5.614872
5.0	0.730100	1.370756	2.234746	3.472919	5.103223	7.230081	5.740295
6.0	0.758344	1.413302	2.305161	3.557316	5.239554	7.295435	5.821551
7.0	0.794778	1.454633	2.346489	3.605906	5.293574	7.353016	9.842359
10.0	0.785584	1.432817	2.392383	3.656030	5.193744	7.217799	5.707064
20.0	0.704902	1.297439	2.343253	3.586895	4.839860	6.768542	5.152162
50.0	0.617707	1.161735	2.152110	3.316916	4.495757	6.334415	8.616733
100.0			1.954410	3.052759			

Reduced Second Virial Coefficient B*(T*,c,a*) for the Hard-Core Morse Potential

Cs 6.00

T*/a*	0.10000	0.30000	0.50000	0.70000	0.90000	1.10000	1.30000
0.25	-1.2211	-25.850411	-34.324192	-42.620764	-51.545585	-61.200735	-71.441529
0.3	-1.236512	-21.473252	-27.332270	-33.767328	-40.670166	-48.060203	-55.847704
0.34	-13.351552	-17.580167	-22.208674	-27.266459	-32.804974	-38.570250	-44.567594
0.36	-11.192640	-14.666902	-18.490902	-22.502642	-26.502879	-31.469795	-36.157541
0.38	-9.531789	-12.425214	-15.567741	-18.906775	-22.463379	-26.012015	-29.760035
0.26	-8.223862	-10.655990	-13.274558	-16.015190	-18.849376	-21.719767	-24.585571
0.4	-7.173082	-9.241046	-11.432913	-13.697500	-15.995605	-18.274335	-20.477760
0.42	-6.314233	-8.082816	-9.920289	-11.790550	-13.664060	-15.461219	-17.179943
0.4	-5.601660	-7.121333	-8.680530	-10.228854	-11.731097	-13.129623	-14.371175
0.46	-5.002716	-6.313261	-7.632193	-8.909706	-10.109216	-11.172238	-12.051987
0.48	-4.493396	-5.626218	-6.741221	-7.786941	-8.730659	-9.509453	-10.079043
0.5	-4.055857	-5.017265	-5.976237	-6.826920	-7.547486	-8.082689	-8.38127
0.55	-3.194564	-3.894418	-4.471831	-4.935682	-5.222082	-5.279346	-5.062270
0.6	-2.563777	-3.025963	-3.371672	-3.553135	-3.552956	-3.231882	-2.534060
0.7	-1.705780	-1.876657	-1.863586	-1.683708	-1.222795	-0.466896	0.64.1329
0.8	-1.161135	-1.140754	-0.937963	-0.465955	0.233387	1.296049	2.754291
0.9	-0.783040	-0.633811	-0.278124	0.331977	1.245049	2.508449	4.170044
1.0	-0.507624	-0.264950	0.197993	0.929743	1.976897	3.388770	5.215181
1.1	-0.293795	0.014484	0.584433	1.381119	2.530387	4.054314	6.001101
1.2	-0.135458	0.232877	0.839957	1.733842	2.962297	4.573510	6.615559
1.3	-0.004508	0.407845	1.065365	2.016094	3.307816	4.988730	7.106025
1.4	0.102608	0.550870	1.249515	2.246560	3.589957	5.327562	7.507613
1.5	0.191699	0.669747	1.402484	2.437411	3.823953	5.608706	7.840009
1.6	0.266843	0.769943	1.531341	2.599028	4.020991	5.845269	8.119794
1.7	0.330982	0.855403	1.641186	2.736316	4.188623	6.046702	8.357693
1.8	0.366293	0.929046	1.735785	2.854505	4.333248	6.219988	8.562601
1.9	0.434418	0.993071	1.817909	2.951157	4.458640	6.370388	8.740383
2.0	0.476618	1.049172	1.889975	3.047016	4.568357	6.501947	8.895782
2.2	0.546904	1.142606	2.009764	3.196450	4.750706	6.720493	9.152029
2.4	0.603100	1.217006	2.105030	3.315182	4.895469	6.893878	9.358435
2.6	0.648707	1.277371	2.182233	3.411303	5.012568	7.034634	9.523723
2.8	0.686352	1.327117	2.245771	3.490323	5.108764	7.149673	9.659902
3.0	0.717832	1.366644	2.298737	3.556117	5.188164	7.244699	9.771924
3.2	0.744645	1.403687	2.343368	3.611491	5.256040	7.325034	9.860769
3.4	0.767156	1.433534	2.391321	3.658518	5.313116	7.393129	9.940548
3.6	0.786693	1.459158	2.413849	3.697367	5.361912	7.451288	10.014890
3.8	0.803618	1.481366	2.441915	3.733446	5.403902	7.501284	10.073504
4.0	0.818368	1.500564	2.466273	3.764495	5.440238	7.544699	10.124222
4.2	0.831292	1.517395	2.487518	3.789601	5.471833	7.582630	10.168248
4.4	0.842669	1.532171	2.506179	3.812541	5.499419	7.614755	10.206579
4.6	0.852724	1.545194	2.522493	3.832621	5.523587	7.643385	10.240017
4.8	0.861643	1.556710	2.536928	3.850297	5.544823	7.668503	10.269339
5.0	0.869580	1.566925	2.549696	3.865896	5.563527	7.690589	10.295084
6.0	0.89835	1.603561	2.595001	3.920918	5.629066	7.767532	10.384310
7.0	0.915297	1.624589	2.620555	3.951196	5.664510	7.808501	10.431170
8.0	0.924347	1.646020	2.644114	3.976632	5.691575	7.836944	10.460470
10.0	0.917188	1.614832	2.594781	3.909635	5.593396	7.712663	10.303640
20.0	0.907285	1.495360	2.426037	3.479316	5.303200	7.345689	10.054785
100.0	0.761604	1.378604	2.262347	3.400834	5.022266	6.990004	9.424770

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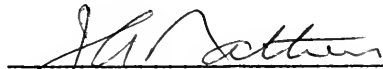114. Johnston, H. L. and Grilly, E. R., J. Phys. Chem. 46, 948(1942).

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BIOGRAPHICAL SKETCH

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.
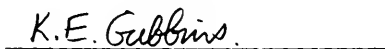
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